Title

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Journal

Deep Sea Research Part II Topical Studies in Oceanography, 53(5-7)

ISSN

0967-0645

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Publication Date

2006-03-01

DOI

10.1016/j.dsr2.2006.01.025

ELSEVIER

Deep-Sea Research II 53 (2006) 459–512

DEEP-SEA RESEARCH
PART II

www.elsevier.com/locate/dsr2

Pelagic functional group modeling: Progress, challenges and prospects

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Received 1 November 2004; accepted 30 January 2006

Abstract

In this paper, we review the state of the art and major challenges in current efforts to incorporate biogeochemical functional groups into models that can be applied on basin-wide and global scales, with an emphasis on models that might ultimately be used to predict how biogeochemical cycles in the ocean will respond to global warming. We define the term "biogeochemical functional group" to refer to groups of organisms that mediate *specific* chemical reactions in the ocean. Thus, according to this definition, "functional groups" have no phylogenetic meaning—these are composed of many different species with common biogeochemical functions.

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0967-0645/$ - see front matter
doi:10.1016/j.dsr2.2006.01.025

Substantial progress has been made in the last decade toward quantifying the rates of these various functions and understanding the factors that control them. For some of these groups, we have developed fairly sophisticated models that incorporate this understanding, e.g. for diazotrophs (e.g. *Trichodesmium*), silica producers (diatoms) and calcifiers (e.g. coccolithophorids and specifically *Emiliania huxleyi*). However, current representations of nitrogen fixation and calcification are incomplete, i.e., based primarily upon models of *Trichodesmium* and *E. huxleyi,* respectively, and many important functional groups have not yet been considered in open-ocean biogeochemical models. Progress has been made over the last decade in efforts to simulate dimethylsulfide (DMS) production and cycling (i.e., by dinoflagellates and prymnesiophytes) and denitrification, but these efforts are still in their infancy, and many significant problems remain.

One obvious gap is that virtually all functional group modeling efforts have focused on autotrophic microbes, while higher trophic levels have been completely ignored. It appears that in some cases (e.g., calcification), incorporating higher trophic levels may be essential not only for representing a particular biogeochemical reaction, but also for modeling export. Another serious problem is our tendency to model the organisms for which we have the most validation data (e.g., *E. huxleyi* and *Trichodesmium*) even when they may represent only a fraction of the biogeochemical functional group we are trying to represent.

When we step back and look at the paleo-oceanographic record, it suggests that oxygen concentrations have played a central role in the evolution and emergence of many of the key functional groups that influence biogeochemical cycles in the present-day ocean. However, more subtle effects are likely to be important over the next century like changes in silicate supply or turbulence that can influence the relative success of diatoms versus dinoflagellates, coccolithophorids and diazotrophs. In general, inferences drawn from the paleo-oceanographic record and theoretical work suggest that global warming will tend to favor the latter because it will give rise to increased stratification. However, decreases in pH and Fe supply could adversely impact coccolithophorids and diazotrophs in the future.

It may be necessary to include explicit dynamic representations of nitrogen fixation, denitrification, silicification and calcification in our models if our goal is predicting the oceanic carbon cycle in the future, because these processes appear to play a very significant role in the carbon cycle of the present-day ocean and they are sensitive to climate change. Observations and models suggest that it may also be necessary to include the DMS cycle to predict future climate, though the effects are still highly uncertain. We have learned a tremendous amount about the distributions and biogeochemical impact of bacteria in the ocean in recent years, yet this improved understanding has not yet been incorporated into many of our models.

All of these considerations lead us toward the development of increasingly complex models. However, recent quantitative model intercomparison studies suggest that continuing to add complexity and more functional groups to our ecosystem models may lead to decreases in predictive ability if the models are not properly constrained with available data. We also caution that capturing the present-day variability tells us little about how well a particular model can predict the future. If our goal is to develop models that can be used to predict how the oceans will respond to global warming, then we need to make more rigorous assessments of predictive skill using the available data.

Keywords: Biogeochemical modeling; Nitrogen fixation; Denitrification; Silica production; Calcification; Dimethylsulfide production

1. Introduction

The biologically mediated fluxes of elements between the upper ocean and the ocean interior are critically dependent upon key groups of organisms. Similarly, fluxes between the atmosphere and ocean, within the ocean and between the ocean and the lithosphere are mediated by organisms that catalyze phase state transitions from either gas to solute/solid or from solute to solid/gas phases. For example, autotrophic carbon fixation converts gaseous CO_2 to a wide variety of organic carbon molecules, virtually all of which are solid or dissolved solids at physiological temperatures. Respiration accomplishes the reverse. Denitrification reduces nitrate-N to N_2; nitrogen fixation reduces N_2 to ammonium-N (and then to organic molecules); ammonia oxidation converts ammonium-N to nitrate-N. Calcification converts dissolved inorganic carbon and Ca to solid-phase calcite and aragonite whereas silicification converts soluble silicic acid to solid hydrated amorphous opal.

Each of these biologically catalyzed processes is dependent upon specific metabolic sequences (i.e., gene families encoding a suite of enzymes) that evolved over hundreds of millions of years of Earth's history, and have, over corresponding periods, had a profound impact on the chemical composition of the oceans and have led to the

massive accumulation of calcite, opal and organic matter in the lithosphere. These metabolic sequences are frequently associated with several groups of organisms (Falkowski and Raven, 1997). Based on their biogeochemical metabolism, these homologously similar sets of organisms can be clustered into "functional groups" or "biogeochemical guilds" following Totterdell et al. (1993) and Falkowski et al. (2003).

It is important to emphasize that "functional groups" have no phylogenetic meaning—these are composed of many evolving entities (species) with common biogeochemical and/or ecological functions but diverse evolutionary origins (see also Le Quere et al., 2005). Using calcifiers as an example, we see that globally significant rates are sustained not only by several different phytoplankton (coccolithophorid) species, but also by zooplankton (foraminifera and pteropods) and reef building (coral) species. This fact poses a major challenge for the biogeochemical modeling community because it implies that we may need to dynamically represent a wide range of calcifying organisms in our models in order to predict calcification rates in the future. This problem is particularly vexing when one considers that multiple species *and* multiple trophic levels are involved. Moreover, we have the same fundamental problem with virtually all of the functional groups under consideration here, e.g., silicification involves many different diatom, silicoflagellate and radiolarian species; nitrogen fixation involves *Trichodesmium*, symbiotic diazotrophs and potentially hundreds of different microbial diazotrophic groups, etc. In order to deal with this level of complexity, it is necessary to identify which organisms and processes contribute significantly to the biogeochemical functions we are attempting to model, versus those that can be ignored or lumped with others. This also demands that research questions be very clearly defined so that relevant (and irrelevant) organisms and processes can be determined.

In our efforts to simulate biogeochemical cycles in the ocean, we are therefore faced with the problem of having to represent not only different functional groups in our models, but also the net effect of a large number of species and multiple trophic levels within each. Thus, when we develop a model we must address two distinct questions: The first is what biogeochemical functions need to be represented? The answer to this question, of course, depends on the application. If the goal is to develop a model that can be used to predict the impact of global warming on biogeochemical cycles in general, then we may be faced with a daunting challenge, i.e., we may need to somehow represent the impact of all of the major biogeochemical functional groups in the ocean. In contrast, if our focus is on the effects of, say, N_2 fixation on primary production and export, then the task is more tractable.

The second question is whether each of these different biogeochemical guilds, which may include hundreds of different species and multiple trophic levels, can be represented by a tractable number of representative groups or species? For example, can open-ocean calcification be modeled by including two generic "species", i.e., one to represent all coccolithophorids and the other all forams? If we choose to use traditional ecosystem modeling approaches, it is probably safe to assume that this kind of simplification will be necessary because we cannot include every calcifying species in the ocean. But can this approach yield a model that reproduces the net calcification effect of a large number of calcifying species? If we are talking about developing models that are going to be used to predict the future, then we must confront an even greater challenge, i.e., predicting how multiple species that carry out these biogeochemical functions will respond to changes in their physical and chemical environment. Over decadal time scales, applying currently observed responses to environmental variability is probably sufficient. However, if we wish to predict variations in global climate over geological time scales then evolution also must be considered.

Alternatively, we can play devil's advocate and ask whether we really need to explicitly include functional groups in our models. Many models simulate the remineralization of organic matter without including heterotrophic bacteria even though bacteria are one of the primary agents of remineralization in the ocean. Similarly, the Martin curve (Martin et al., 1987) can be used to parameterize the remineralization of sinking organic matter throughout the water column without explicitly including the organisms involved. Is it possible that one could model biogeochemical cycles in different strata in the ocean, i.e., the euphotic zone, the mesopelagic, etc., by just treating the strata as black boxes into which one introduces nitrogen, phosphorus, iron, silicate, mixed-layer depth and sunlight, and out of which come DOC, particulate organic carbon (POC), silica and

calcium carbonate in amounts and proportions determined by some empirical algorithm that seeks to minimize the difference between the model estimates and the available observations? Given the magnitude of the challenges we face in trying to represent a vast array of biogeochemical functions in mechanistic models, perhaps these kinds of empirical approaches should be considered more seriously. A litmus test for mechanistic biogeochemical models might be whether or not they can do a better job of describing data than an empirical model with the same number of degrees of freedom. However, one must also consider that an important role of biogeochemical modeling in ocean science is to test and improve our knowledge of processes, which is a priori eliminated by adopting an empirical approach. Moreover, the reality is that mechanistic models tend to have far more parameters (degrees of freedom) than the simpler empirical models, and so in theory can be calibrated to fit particular datasets more easily. Perhaps the most pressing need is for more rigorous validation of our models (as opposed to calibration), using independent datasets that quantitatively assess predictive skill.

In this paper, we review the state of the art and major challenges in our current efforts to incorporate specific biogeochemical functional groups into ocean biogeochemical models. The groups considered here include diazotrophs, denitrifiers, silica producers, calcifiers and dimethylsulfide (DMS) producers. In addition, we address several overarching questions in this review. For example, what are the factors that drive diversity between functional groups in the ocean and what does the paleoceanographic record tell us about how these factors might change in the future? How important is the role of higher trophic levels in determining the expression of different biogeochemical functions? What are the prospects for our current modeling approaches and what new modeling tools can we apply to meet this challenge?

We show that substantial progress has been made in functional group modeling over the last 10 years. For example, dynamic representations of nitrogen fixation, silicification and calcification are now routinely included in ocean biogeochemical models, and it appears that these functional group models reproduce present-day variability reasonably well. However, for some functional groups our models are still crude and/or they are still evolving (e.g., denitrification and DMS production) and for others we have ignored important organisms that mediate the function (e.g., calcifying foraminifera). For all of these groups, the availability of species-level physiological, ecological and/or rate validation data has been a limiting factor in model development. We conclude that major gaps remain in our models and our understanding, and we suggest that using traditional, multi-species ecosystem modeling approaches to develop ever more complicated models may not lead to improved predictive skill.

2. State of the art in functional group modeling and understanding

In this section, we review current efforts to incorporate functional groups into biogeochemical models. We variously consider the state of our knowledge, the state of the art in modeling and future prospects. Obviously, there are many important marine biogeochemical reactions that are not considered, for example, sulfate reduction and other transformations that occur under low-oxygen conditions in the water column and in the sediments. We focus primarily on pelagic biogeochemistry and prognostic models that can be applied on basin-wide and global scales in coupled, three-dimensional applications, i.e., models that might ultimately be used to predict how biogeochemical cycles in the ocean will be altered by climate change and global warming.

2.1. N_2 fixation

2.1.1. State of our knowledge

The potential importance of nitrogen fixation (Fig. 1) in the open ocean has been recognized for half a century, beginning with the discovery by Dugdale et al. (1964) that the conspicuous cyanobacterium, *Trichodesmium,* is diazotrophic. Research in the 1980s and early 1990s (Carpenter and Capone, 1992) suggested that N_2-fixation rates associated with this organism were relatively low. More recent geochemical studies based upon "*N* star" (N^*) anomalies (see Section 3.2 for a mathematical definition of this derived parameter) have suggested much higher rates, i.e., on the order of 20–40 Tg N/y for the North Atlantic (Michaels et al., 1996; Gruber and Sarmiento, 1997) and 80–160 Tg N/y globally (Gruber and Sarmiento, 1997), and direct rate estimates have been revised upward as well (e.g. Galloway et al., 2004; Capone et al., 2005). However, there is still some uncertainty

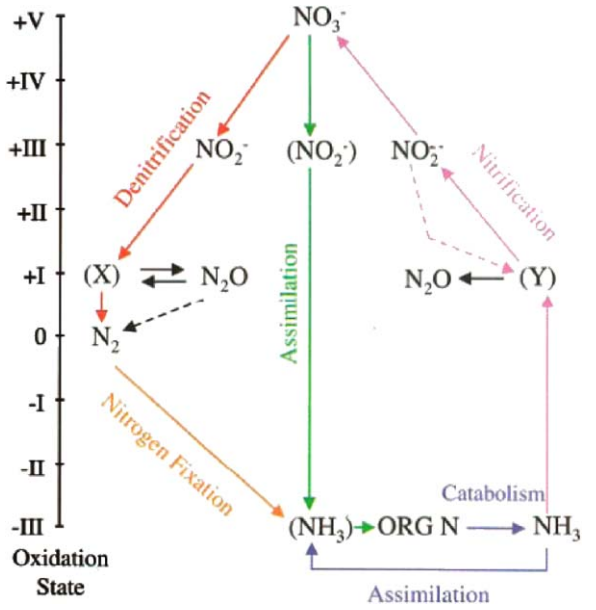

Fig. 1. Simplified schematic diagram of the nitrogen cycle showing the oxidation state of the various forms of N. Reprinted with permission from Codispoti et al. (2001). © 2001, Scientia Marina.

and debate about both the geochemical and the direct rate estimates (see, for example, Hansell et al., 2004).

Discrepancies between direct N_2-fixation rate estimates based upon *Trichodesmium* (e.g. Capone et al., 1997) and higher geochemical estimates (Michaels et al., 1996; Gruber and Sarmiento, 1997) may be reconciled by the contributions from other groups of N_2 fixers (Hood et al., 2000; Capone et al., 2005). For example, the symbiotic species *Richelia intracellularis*, which grows in association with diatoms like *Hemiaulus* spp., contributes significantly to N_2 fixation in areas where there are significant riverine influences (Capone et al., 2005). Moreover, epifluorescence and light microscopy and molecular probes have recently revealed a large and diverse microbial community of potential N_2 fixers in the open ocean (Zehr et al., 2001). Rate estimates from both the Atlantic and Pacific suggest that N_2 fixation associated with these other diazotrophic communities can be comparable to those associated with *Trichodesmium* (Montoya et al., 2004; Capone et al., 2005). There is now also evidence of significant interannual variability in open-ocean N_2 fixation, perhaps associated with climatic oscillations like ENSO and the NAO (Hood et al., 2001; Karl et al., 2001; Bates and Hansell, 2004).

The factors that control *Trichodesmium* growth are thought to include temperature, stratification, competition with other phytoplankton species and the availability of iron and/or phosphorus. Temperature control has been inferred from the observation that *Trichodesmium* is not found in significant densities in waters that are colder than 20 °C, and rarely blooms below 25 °C (Carpenter and Capone, 1992; Capone et al., 1997; Subramaniam et al., 2002). The importance of stratification has similarly been deduced from reports that *Trichodesmium* blooms develop under calm conditions and dissipate rapidly when winds begin to increase (Subramaniam et al., 2002). Hood et al. (2001) and Hood et al. (2004) suggested that, because *Trichodesmium* has a high energy requirement, it must have stratification and high light levels to maximize its growth rate, whereas deep mixing results in lower light levels and entrainment of nitrate from depth, which favors the growth of non-diazotrophic phytoplankton. Alternatively, the empirical evidence linking *Trichodesmium* blooms with stratification may be an artifact. High concentrations of *Trichodesmium* may appear near the surface under stratified conditions because the absence of turbulence allows the positively buoyant trichomes to accumulate.

There are also several lines of evidence that suggest that iron and/or phosphorus play significant roles in controlling N_2-fixation rates in the open ocean. Because of the high Fe requirement of the nitrogenase enzyme and the global correspondence between regions of iron deposition and N_2 fixation, it is generally thought that diazotrophic growth is limited by the availability of iron (Rueter, 1982; Raven, 1988; Rueter et al., 1992; Paerl, 1999; Berman-Frank et al., 2001). However, the degree to which Fe limits *Trichodesmium* growth is still an open question (Hood et al., 2000) and the evidence for phosphorus limitation is also mixed (Sanudo-Wilhelmy et al., 2001; Dyhrman et al., 2002). Recent experimental work in the eastern subtropical Atlantic suggests that *Trichodesmium* growth and N_2 fixation are co-limited by iron and phosphorus (Mills et al., 2004). In contrast, recent modeling studies in the Atlantic (Hood et al., 2001, 2004; Coles et al., 2004) suggest that stratification and mixing provide the first-order controls on *Trichodesmium* growth and biomass distributions. It is probably reasonable to conclude that both physical and chemical factors play important roles in determining the rates and the distribution patterns

of diazotrophs in both the Atlantic and the Pacific. However, the potential for Fe limitation is much greater in the Pacific, where atmospheric Fe deposition is much lower (Tegen and Fung, 1995; Husar et al., 1997). In contrast, the potential for P limitation of N_2 fixation appears to be greater in the Atlantic, i.e., N:P ratios are significantly higher in the Sargasso Sea than in the North Pacific in the vicinity of the Hawaii Ocean Time-series (HOT) station (Wu et al., 2000; Ammerman et al., 2003).

Compared to *Trichodesmium*, we know very little about the factors that control other N_2 fixers in the ocean. The microbial diazotrophs are particularly relevant because they grow in open-ocean waters like *Trichodesmium*, and they can account for comparable rates of N_2 fixation (Montoya et al., 2004; Capone et al., 2005). It is almost certainly true that microbial diazotrophs are subject to very different physiological and ecological constraints (i.e., intensity of grazing pressure, susceptibility to Fe limitation, sinking rates, etc.). Yet it appears that both groups (and diazotrophs in general) are favored by increased stratification and oligotrophic conditions (J. Montoya, personal communication).

2.1.2. State of our models

Efforts to incorporate N_2 fixation into open-ocean biogeochemical models began in the late 1990s. Early examples include models developed by Bissett et al. (1999a, b), Tyrrell (1999), Neumann (2000), Hood et al. (2001), Fennel et al. (2002) and Moore et al. (2002a, b). The Bissett et al. (1999a, b) model does not include an explicit representation of diazotrophic biomass. Rather, it accounts for N_2 fixation as a flux to the dissolved organic-matter pool using a simple paramaterization which assumes that N_2-fixation rate is proportional to temperature and irradiance. In contrast, Hood et al. (2001) modeled *Trichodesmium* biomass in a mixed layer explicitly assuming that N_2-fixation rate is dependent upon light, which is regulated by mixed-layer depth/stratification. In subsequent studies, Hood et al. (2004) and Coles et al. (2004) coupled this model to a three-dimensional circulation model of the tropical and subtropical Atlantic. An obvious deficiency in both the Bissett et al. (1999a, b) and Hood et al. (2001) models is that they do not include phosphorus or iron limitations.

Tyrrell (1999) developed a simplified box model with both nitrogen and phosphorus cycling where the N_2-fixation rate is a function of the supply ratio of inorganic nitrogen and phosphorus. The underlying assumption of this model is that diazotrophs become dominant when reactive nitrogen concentrations become low relative to Redfield N:P. In a three-dimensional model developed by Neumann (2000), N_2-fixation rate depends upon phosphorus supply, temperature and irradiance. The models of Tyrrell (1999) and Neumann (2000) can distinguish between nitrogen and phosphorus control of phytoplankton and diazotroph growth. However, both assume a fixed Redfield stoichiometry in the organic pools even though large departures from Redfield stoichiometry have been observed in these pools in oceans regions where N_2 fixation is important (Gruber and Sarmiento, 1997; Karl et al., 1997; Ammerman et al., 2003). In contrast, Fennel et al. (2002) developed a one-dimensional model with N_2 fixation and both N and P limitations that allows for different stoichiometric ratios in different organic-matter compartments (i.e., high N:P ratio in diazotrophs) and differential export of nitrogen and phosphorus from the upper ocean. In this regard, the model of Fennel et al. (2002) represents an important step forward. However, they did not provide any mechanism for enhancing phosphorus supply to the surface, e.g., "P-mining" (Karl et al., 1992) or enhanced P recycling (Wu et al., 2000). As a result, the diazotrophs in their model form a subsurface maximum that is associated with the phosphocline rather than growing near the surface.

In two related global modeling efforts, Moore et al. (2002a, b, 2004) included diazotrophs in a multi-species, mutli-element biogeochemical model. Although they include phosphorus and iron limitation of N_2 fixation, the large-scale patterns of diazotrophic biomass and N_2 fixation are similar in the Atlantic to those in Hood et al. (2004), suggesting that these patterns are determined primarily by mixed-layer depth and light, and/or temperature. However, Moore et al. (2002a, b, 2004) also report widespread phosphorus limitation of N_2 fixation in the Atlantic in their model, particularly in Moore et al. (2004), where the N/P ratio is fixed. Like the Fennel et al. (2002) model, the Moore et al. models do not provide any special mechanism to enhance phosphorus supply to support diazotroph and phytoplankton growth. In Moore et al. (2002a, b), the combination of flexible N:P ratios and the application of nutrient restoring terms in the nutricline appears to substantially alleviate phosphorus limitation. Finally, Fe limitation and cycling is explicitly represented in the Moore et al. models using assumptions and simplifications that

are similar to other model applications, e.g., Christian et al. (2002a, b). Diazotrophs are distinguished by their high Fe requirement. Fe is an important global control on nitrogen fixation in the Moore et al. models, with the degree of limitation depending to a large extent upon the specified Fe solubility.

2.1.3. Future directions

Although substantial progress has been made in recent years toward representing N_2 fixation in biogeochemical models, there are still some significant problems and questions. One obvious challenge is the realization that diazotrophs other than *Trichodesmium* are important in the open ocean. Future efforts to simulate N_2 fixation will have to account for these other sources if they are truly significant. However, progress along these lines will require much more information about the physiology, ecology and distribution of these organisms. Including Fe limitation in models with N_2 fixation is, obviously, a major challenge, i.e., there are still very few observations of iron in the ocean and the processes controlling Fe cycling are still poorly understood (e.g., complexation with ligands, solubility/bioavailability of eolian iron, the role of colloid formation, etc.). This challenge, however, is not specific to N_2 fixation. That is, it does not appear to pose any major problems beyond those associated with modeling Fe concentrations and cycling in the pelagic ecosystem in general.

Another significant challenge is understanding and modeling the phosphorus cycle and supply as it relates to N_2 fixation and the nitrogen inventory. Although there is a relatively large database of phosphorus observations (at least for the inorganic form) and P cycling has been studied (and modeled) for many years, there are still many unanswered questions about the role of phosphorus in controlling N_2 fixation and primary production in general (Hood et al., 2000; Wu et al., 2000; Ammerman et al., 2003; Thingstad et al., 2005). As in Fennel et al. (2002), most models that include explicit representations of diazotrophs do not incorporate a means of supplying extra phosphorus for the particulate matter formation associated with N_2 fixation. Phosphorus limitation of N_2 fixation can be relieved by enhancing the rate of phosphorus recycling relative to nitrogen or perhaps through phosphorus mining. These mechanisms, however, provide only a short-term solution to the problem. Ultimately, denitrification must be invoked to keep N:P ratios in check. Obviously, if we include N_2 fixation in long-term climate simulations, we must also include denitrification and ammonia oxidation to complete the redox cycle. At present, the specific factors and feedbacks that control the relative global rates of N_2 fixation and denitrification are a matter of debate (Wu et al., 2000).

2.2. Denitrification

2.2.1. State of our knowledge

Denitrification in the world oceans occurs in marine sediments and in suboxic waters (i.e. $O_2 < 5\,\mu M$), the latter typically referred to as an oxygen minimum zone (OMZ), and consists of the use of oxidized nitrogen as an electron acceptor in the oxidation of organic carbon by denitrifying bacteria (Fig. 1). The general sequence of oxidation stages associated with complete denitrification begins with reduction of nitrate (NO_3) to nitrite (NO_2), which is subsequently reduced to nitric oxide (NO), nitrous oxide (N_2O) and, finally, dinitrogen gas (N_2). Significant denitrification occurs in the benthos and several open-ocean regions where persistent OMZs have been observed. Denitrification is carried out by numerous proteobacteria and archaebacteria groups that encompass a wide range of physiological characteristics and ecological functions. However, in spite of this diversity, denitrifiers are unified as facultative anaerobes, i.e., bacteria that respire aerobically in the presence of oxygen and anaerobically in the presence of suitable alternative electron acceptors like nitrate and nitrite (King, 2005). As a result, the potential for denitrification exists in most marine habitats. The enzymes that catalyze the denitrification reactions (nitrogen oxide reductases) are repressed by O_2. These enzymes are derepressed very rapidly when O_2 is removed, i.e., in minutes to hours (Knowles, 1982). Denitrifying activity is also related to organic carbon and nitrogen oxide substrate availability, to pH with an optimum in the range of 7–8, and there is a marked temperature dependence (Knowles, 1982).

Codispoti et al. (2001) recently ascribed global losses (from the ocean to the atmosphere) of 300 and $150\,Tg\,N\,yr^{-1}$ to benthic and water-column denitrification, respectively. Losses of N from the ocean to the atmosphere due to benthic denitrification have undergone significant upward revision over the past two decades (see Codispoti and Christensen, 1985) with a good portion of this

coming from continental margins that are susceptible to ongoing eutrophication resulting from anthropogenic nitrate loading in runoff waters (Naqvi et al., 2000). The open-ocean regions where significant water-column denitrification occurs include portions of the eastern tropical North Pacific (ETNP, Cline and Richards, 1972; Codispoti and Richards, 1976), the eastern tropical South Pacific (ETSP, Codispoti and Packard, 1980) and the Arabian Sea (Naqvi, 1987; Morrison et al., 1999). Significant water-column denitrification also may occur in the Benguela upwelling system; however, rate estimates are as yet not forthcoming (Tyrrell and Lucas, 2002).

As noted in the previous section, there is still considerable uncertainty in the global ocean nitrogen budget, i.e., the degree to which N inputs into the ocean due to nitrogen fixation are balanced by N losses associated with denitrification, nitrification and other reactions associated with the oxidation of ammonia (see also Section 3.2 below, Fig. 2). For example, Codispoti et al. (2001) have suggested that in the present-day ocean N losses may exceed inputs by as much as $200\,\mathrm{Tg\,N\,yr^{-1}}$. It has been argued that the imbalances between these two processes are inherently self-correcting (Tyrrell, 1999). That is, excess denitrification will ultimately lead to N limitation, which will promote N_2 fixation in tropical and subtropical waters, while excess N_2 fixation will ultimately lead to phosphorus limitation, which will result in a negative feedback on itself. However, since areas of elevated denitrification and nitrogen fixation are not collocated, circulation pathways set a fairly long characteristic time scale for the first of these two feedbacks, which Codispoti (1989) has estimated to be $O(10^3)$ years. Thus, significant imbalances may develop and persist for tens and perhaps even hundreds of years and these could have significant carbon cycle implications through their influence on the biological pump. For example, Falkowski (1997) estimated that if a loss of $70\,\mathrm{Tg\,N\,yr^{-1}}$ due to denitrification were directly applied as a decrease in new production, the oceanic drawdown of atmospheric CO_2 would be reduced by $70\,\mathrm{MT\,C\,yr^{-1}}$.

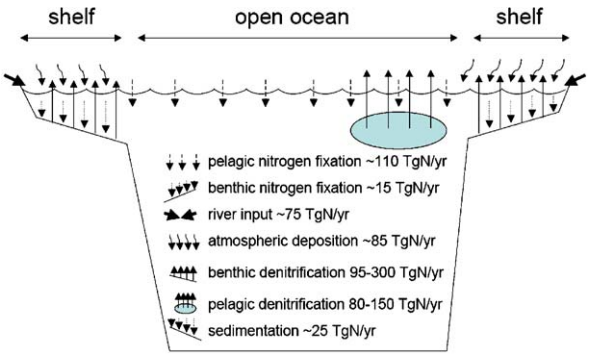

Fig. 2. Schematic diagram illustrating the ocean N-budget with major N source and sink terms and their relative spatial distributions (values are combined estimates from Gruber and Sarmiento, 1997; Codispoti et al., 2001).

Another impact on global climate associated with denitrification is production of N_2O, which is an important greenhouse gas (its contribution to radiative forcing ranks behind only that of CO_2 and methane; Ramaswamy et al., 2001). At present, efflux from the marine environment is thought to represent ~30% of the total natural source for atmospheric N_2O, which is estimated to be $9.6\,\mathrm{Tg\,N\,yr^{-1}}$ (Prather et al., 2001). Since both nitrification and denitrification produce N_2O, questions persist as to the relative contributions of these two processes to the overall oceanic source. While the mechanisms of oceanic N_2O production are not yet fully comprehended, the evidence supporting a prominent contribution by pelagic denitrification is compelling and continues to accumulate.

2.2.2. *State of our models*

Clearly, our understanding of the magnitude of oceanic denitrification, and the specific biogeochemical processes associated with it, is still evolving. This is reflected in the present state-of-the-art in pelagic marine denitrification modeling, i.e., open-ocean modeling efforts to date have been relatively crude in many respects. This apparent lack of progress is not due to an absence of a chemical, mathematical or numerical foundation for modeling denitrification (Fennel and Neumann, 2004). Numerous models that include denitrification have been developed and applied in inland seas, coastal and benthic systems. Denitrification has not been included in many open-ocean N-cycle models because in many regions, and over shorter time scales, its impact on the N inventory can be assumed to be negligible. But another factor is the difficulty inherent in simulating organic-matter loading and oxygen concentrations in hypoxic/anoxic mesopelagic regions (i.e., OMZs), which are pre-requisites for making a truly prognostic denitrification rate calculation. And there is also the practical constraint that any attempt to model all of the denitrification in the ocean must account for it in

open-ocean OMZs and also shelf/slope waters. Most general circulation models (GCMs) applied at basin and global scales do not resolve the continental shelves.

Nonetheless, Anderson et al. (1982) presented an early modeling study that investigated nitrate deficits and the secondary nitrite maxima that result from denitrification regions in OMZs in the Arabian Sea, ETNP and coastal waters off Peru. They integrated the 1-D form of an advective-diffusion-reaction equation set that tracked nitrate and nitrite. Rates were specified for nitrification and the consumption of nitrate and nitrite by denitrification, with nitrite being reduced directly to N_2 (Fig. 1). An additional simplification consisted of characterizing the OMZ as a two-layer system with a denitrifying layer overlying a nitrifying layer. Their results indicated that the lack of coincidence in the depth of the nitrite and nitrate deficit maxima (which characterizes in situ profiles from the ETNP but is not apparent in similar profiles from the ETSP and the Arabian Sea) might be related to the magnitude of export production. In an effort to simulate the nitrification–denitrification linkage noted above, concentrations of nitrate consumed and nitrite produced by denitrification were allowed, via diffusion, to move toward steady state with concentrations in the surrounding oxygenated waters.

We did not include the water-column reducing environment of the Black Sea in our discussions above because of its relatively minor contribution to global losses of fixed nitrogen. However, several important modeling efforts have been focused on its low-oxygen environment. For example, Yakushev and Neretin (1997) developed a 1-D advective-diffusion-reaction model, similar to that of Anderson et al. (1982), to study chemical transformations in the low-oxygen regions of the Arabian Sea and the Black Sea. Oxygen-dependent cycling of both sulfur and nitrogen in the marine environment was included in their model, with denitrification again being represented by the transformation of nitrate to nitrite to dinitrogen gas (Fig. 1). Here, the transition from denitrification to nitrification between the anoxic core and the surrounding oxic waters consisted of linear relations that modified the rate of each process, with O_2 thresholds taken from the available literature. The simulated vertical profiles of nitrogen compounds in the subeuphotic zone of both regions were generally consistent with the observations, and accurate representation of N_2 production primarily depended on the magnitude of turbulent diffusivity and the load of organic matter applied as an upper boundary condition.

A subsequent effort, which focused solely on the Black Sea, consisted of coupling modules for biological production, nitrogen cycling and redox cycling to a turbulence closure model and once again nitrite was included as an intermediate byproduct of denitrification (Oguz et al., 2000). In this case, hyperbolic saturation functions (Monod functions) were applied as a means of transitioning between nitrification and denitrification. This model represents a significant advancement in simulating the linkage between nitrifying and denitrifying regimes as both mixing and export production from the overlying euphotic zone were interactive/dynamic components of the modeling scheme. Vertical distributions of nitrate and nitrite as a function of density anomalies showed excellent agreement with in situ profiles, including the subsurface nitrate maximum above suboxic waters and the location of the secondary nitrite maximum within these suboxic waters

In an effort to assess oceanic source mechanisms of this greenhouse gas, Suntharalingam and Sarmiento (2000) and Suntharalingam et al. (2000) coupled a simple N_2O production model to a coarse resolution ocean GCM. The production of N_2O was formulated as a function of oxygen consumption, i.e., it was assumed to be proportional to remineralization of organic matter, and therefore to nitrification. Based on studies of ammonia-oxidizing bacteria in culture, a dependence of N_2O yield on O_2 concentration was introduced in their latter effort. Among other things, they found that the best comparison to zonally integrated distributions of N_2O flux occurred when 25% of the N_2O originated from suboxic regions.

It is interesting to note that none of these modeling efforts involve explicit representation of the bacteria that are responsible for denitrification (or nitrification). Rather, it is assumed that they are ubiquitous and that the reactions will occur if the conditions allow the relevant enzymes to function. In contrast, many current efforts to model N_2 fixation (Section 2.1), silicification (Section 2.3), calcification (Section 2.4) and DMS production (Section 2.5) involve explicit (or quasi-explicit in the case of DMS) representation of the organisms that are involved. This tactic of "parameterizing" the causative organisms is often taken when representing bacterially mediated reactions in biogeochemical

models (see Section 3.5). The reasons for doing this are varied, but as we suggest below may stem largely from the fact that we have relatively little specific information about the physiology, ecology and variability of bacteria biomass and community composition compared to the phytoplanktonic species that mediate these other biogeochemical functions.

2.2.3. Future directions

A key issue in including denitrification within biogeochemical models designed to simulate nitrogen transformations within the pelagic environment is how to handle the nitrification–denitrification linkage. The efforts of Yakushev and Neretin (1997) and Oguz et al. (2000), respectively, employ linear and hyperbolic forms of O_2-dependent relations to capture the transition between the two processes, with only the former effort providing an overlap regime. None of the published efforts explicitly accounts for N_2O production/consumption in the anoxic breakdown of nitrite, a significant shortcoming given its role in global climate. The attempt of Suntharalingam et al. (2000) was specifically directed at ascertaining the importance of OMZ-produced N_2O. However, they were hampered by a need for better-resolved observations for validation, and they used annually averaged wind stress, so potential impacts of monsoon forcing on the Arabian Sea OMZ were not included.

Redfield's stoichiometry for dentrification (e.g., Richards, 1965) has been assumed to be applicable for all the modeling efforts noted above. However, there is growing evidence that this is simply not the case. For example, Van Mooy et al. (2002) reported that under anoxic conditions nitrogen-rich amino acids within sinking particulate matter are preferentially utilized as organic substrate for denitrification. Their alternative stoichiometry implies that losses of fixed nitrogen due to denitrification, as estimated by Gruber and Sarmiento (1997) or Deutsch et al. (2001), are under-represented by 9%. Furthermore, the anaerobic ammonium oxidation (anammox) reaction, which consists of the oxidation of ammonium with nitrite, has been proposed as a likely pathway for globally significant losses of fixed nitrogen (Codispoti et al., 2001). This reasoning is supported by a recent study that ascribes 19–35% of areal formation of N_2 in anoxic waters off Costa Rica to the anammox reaction (Dalsgaard et al., 2003). Application of a phylogenetic analysis to bacteria in the Black Sea by Kuypers et al. (2003) has confirmed the presence of bacteria capable of the annamox process. These investigators found that these bacteria are abundant within the nitrite peak of the Black Sea water column, and they argued that the coupling of nitrite formed by denitrification and the anammox reaction leads to a significant loss of fixed nitrogen. In another recent study, Granger and Ward (2003) demonstrated that trace metals can influence N_2O production in OMZs.

Certainly, the modeling efforts to date have provided substantial insights into the relative contributions of various processes associated with oceanic denitrification. All have been ground breaking and have served to emphasize our need to better understand denitrification in the marine environment. However, these efforts must be considered preliminary. At present, there are very few large-scale biogeochemical models that incorporate dynamic/prognostic representations of denitrification, and those that do, do not involve explicit representations of denitrifying bacteria. Whether or not the latter is necessary is an open question. New findings relating to dentrification and N-cycle processes in general, and our growing realization of their potential role in the carbon cycle and climate, emphasize the need for continued research and model development along these lines.

2.3. Silica producers

2.3.1. State of our knowledge

In this section, we turn out attention away for the nitrogen cycle and focus on silica production and diatoms in particular (we note, however, that amorphous silica is also produced in the upper ocean by silicoflagellates and radiolarians, which are discussed briefly at the end of this section). Diatoms tend to be somewhat larger and faster growing than other phytoplankton groups, and to be adapted to more nutrient-rich habitats. These properties often cause diatoms to dominate phytoplankton blooms in coastal waters and the open ocean (Guillard and Kilham, 1978; Nelson et al., 1995). The diatoms' importance as bloom-forming organisms makes them major contributors to primary production, new production and organic-matter export in the ocean, and biogeochemical models of upper-ocean processes often seek to include diatoms explicitly as a functional group whose properties differ from those of other

phytoplankton groups (e.g. Walsh, 1975; Chai et al., 2002).

There is, however, considerable overlap between the diatoms and other phytoplankton groups with respect to size, maximum growth rate and general nutrient (N, P and Fe) requirements. The most significant qualitative difference between the diatoms and other functional groups in the phytoplankton is the diatoms' growth requirement for Si. Unlike other groups, diatoms deposit silica $(SiO_2)_{bio}$ within their cell walls and must take up dissolved Si in order to form the new cell wall and divide (Lewin, 1962; Brzezinski et al., 1990). This Si uptake can deplete dissolved Si to levels low enough to limit rates of diatom growth and photosynthesis (Nelson and Dortch, 1996; Nelson et al., 2001). Biogeochemical models seeking to simulate diatom growth and productivity must therefore take their Si requirement into account by including an Si cycle and the potential for Si limitation (Dugdale et al., 1995; Pondaven et al., 1998; Chai et al., 2002).

The oceanic Si cycle is considerably simpler and thus better understood than the cycles of N, P and Fe. Dissolved Si is present in seawater almost exclusively as silicic acid ($Si(OH)_4$), which at seawater pH is ~5% dissociated to $SiO(OH)_3^-$ with all further dissociation products comprising <0.01% of the total (Stumm and Morgan, 1996). Acid–base equilibria among $Si(OH)_4$ and its dissociation products is reached rapidly enough that their aggregate concentration is measured in all widely used chemical analyses, and hence they can be considered ecologically as a single nutrient pool. There are also no known volatile or organic forms of dissolved Si in seawater.

Uptake of $Si(OH)_4$ by diatoms is similar to uptake of dissolved N and P by other phytoplankton groups in that it follows Michaelis–Menten kinetics, with K_S values usually between 1 and 5 μM for natural diatom assemblages in a wide range of ocean habitats (Nelson and Treguer, 1992; Leynaert et al., 2001; but see also the very high values reported by Sommer, 1986, 1991). Both detrital $(SiO_2)_{bio}$ and silica in the cell walls of living diatoms dissolve spontaneously in seawater, which is significantly undersaturated with respect to $(SiO_2)_{bio}$ (Stumm and Morgan, 1996). Detrital $(SiO_2)_{bio}$ dissolves 5–10 times faster than diatom $(SiO_2)_{bio}$ because living diatoms protect the silica in their cell walls with an organic coating that can be degraded by bacterial attack after the cell dies (Bidle and Azam, 1999, 2001). This distinction between the dissolution rates of living and detrital $(SiO_2)_{bio}$ appears to be important for modeling $Si(OH)_4$ regeneration in the ocean. Other biological factors, such as diatom species composition, cell morphology and aggregation (Nelson et al., 1995; Brzezinski et al., 1997) also play a role in determining the Si cycle in the ocean, but their effects are not yet understood well enough to be parameterized well in biogeochemical models.

Due to the larger size of diatoms and greater density of their siliceous cell walls, particles containing either cellular or detrital $(SiO_2)_{bio}$ tend to sink faster than other organic particles (Smetacek, 1985, see also Section 3.3 below). In spite of the thermodynamic tendency for biogenic opal to dissolve in seawater, opal is one of the three main constituents in deep-sea sediments (along with calcite and the products of terrestrial weathering). The preservation of opal in sediments is controlled by competing kinetics of dissolution and removal from undersaturated seawater by burial. Because of this kinetic competition, sediments with high opal concentration tend to be found in regions of high opal productivity, such as in the southern ocean. In the tropics, surface sediments often contain ~5–20% opal by weight.

Marine diatoms growing under nutrient-replete conditions tend to have molar Si:N ratios ~1.0, and Si:C ratios ~0.15 (Brzezinski, 1985). There are, however, many circumstances in which it is inappropriate to assume fixed Si:N or Si:C ratios. Although diatoms must deposit $(SiO_2)_{bio}$ within their forming cell wall in order to divide, diatoms growing under severe Si limitation can diminish the amount of Si in the cell wall by at least a factor of five (Paasche, 1973; Brzezinski et al., 1990), substantially decreasing their cellular Si:N ratio. Ecologically, this permits diatoms to grow and produce organic matter at significant rates even when $[Si(OH)_4] \ll K_S$. Similarly, diatoms growing under severe N limitation produce less organic matter per cell, which can diminish their N content per cell to <1/5 of that in N-replete cells (Goldman and McCarthy, 1978). These two effects, taken together, mean that the Si:N ratio of a single diatom species can be 20–30 times higher under severe N limitation than under severe Si limitation.

In addition, it is now clear that Fe limitation strongly affects the Si:C and Si:N ratios of diatoms. When high-nitrate, low-chlorophyll (HNLC) surface waters are low in [Fe], diatoms grow with abnormally high Si:C and Si:N ratios, primarily because of decreased organic-matter content

(Hutchins and Bruland, 1998; Takeda, 1998; Franck et al., 2000). This effect seems to result mainly from the fact that Fe-deficient diatoms have lower photosynthetic efficiency and diminished ability to reduce nitrate for assimilation into organic matter (Sunda and Huntsman, 1997). Davey and Geider (2001) point out that the photosynthetic electron transport (PET) chain accounts for ~80% of the iron required by phytoplankton and conclude that the primary effect of iron limitation is probably a reduction in the rate of PET. The result is an "energy crisis" that limits carbon fixation, pigment accumulation and nitrogen assimilation. Culture studies have indeed shown that additional iron increases diatom growth rates and maximum rates of Si uptake, with little or no effect on K_S (De La Rocha et al., 2000). Diatoms can adjust to iron limitation to some extent. The genome of the diatom *Thalassiosira pseudonana*, for example, contains novel genes for high-affinity iron uptake as well as silicic acid transport and formation of silica-based cell walls (Armbrust et al., 2004). Diatoms in general have the ability to substitute flavodoxin for ferredoxin on the acceptor side of PSI (McKay et al., 1997), and at least in the cases of *Thalassiiosira weissflogii* and *Phaeodactylum tricornutum* grown under continuous illumination, impacts of iron limitation on growth rate are small. Davey and Geider (2001) attribute this behavior to a shift in the rate-limiting step for light-saturated photosynthesis from the Calvin cycle under continuous illumination to PET and possibly PSII function when cells are grown on a light:dark cycle.

2.3.2. State of our models

The fundamental components of the oceanic Si cycle can be represented by a simple three-component model (Fig. 3). In this model, physical processes enrich the euphotic zone with dissolved $Si(OH)_4$, which is utilized by diatoms in their production of biogenic silica $(SiO_2)_{bio}$ as a component of their cellular biomass. Mortality due to grazing and other processes convert some of the diatom silica into detrital $(SiO_2)_{bio}$ and both cellular and detrital $(SiO_2)_{bio}$ dissolve, regenerating $Si(OH)_4$. Thus some fraction of the diatoms' Si requirement is met by physical processes analogous to those that supply "new" NO_3^- to surface waters and some by biologically mediated processes analogous to those that supply "old" or recycled NH_4^+. Both cellular and detrital $(SiO_2)_{bio}$ are also exported to the deep ocean by some combination of gravitational settling, vertical mixing and grazing followed by sinking of zooplankton fecal pellets.

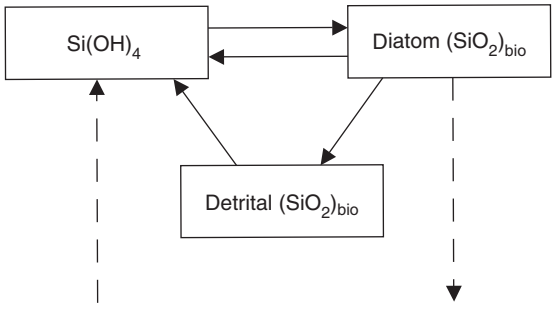

Fig. 3. Essential components of upper-ocean Si cycle model.

Models in which phytoplankton biomass (PB) contains C, N and P in Redfield proportions (106:16:1) often assign diatoms a composition of 106 moles C, 16 moles N and 16 moles Si for each mole of P. To a first approximation, this composition is entirely consistent with data and useful for relating the Si cycle quantitatively to the cycling of organic matter. Several models have yielded realistic distributions and time courses of $[Si(OH)_4]$, SiO_{bio} and the contribution of diatoms to primary productivity using this assumption (Chai et al., 2002; Fujii et al., 2002; Aumont et al., 2003). However, diatoms are capable of considerable compositional flexibility (Davidson and Gurney, 1999). This flexibility enables them to divide at a high fraction of their maximum rate, even when some nutrient (N, Si or Fe) is severely depleted, by simply getting along with less of whatever is in short supply. From a modeling perspective, this flexibility means that diatoms can grow more rapidly, and remain more active metabolically, in surface waters that are low in dissolved N, Si or Fe than one would conclude if one assumed that they must grow with a fixed elemental composition. Models are beginning to incorporate this flexibility by permitting C, N, Si and Fe to be taken up independently, with the result that the elemental composition of the cells changes with time in response to local light and nutrient conditions (Moore et al., 2002,a b; Mongin et al., 2003). Such models track the cellular Si:N, C:N and Fe:C ratios as they change and use them as proxies for cellular C, N, Si and Fe content. The growth rate, and hence the rates at which non-limiting nutrients are taken up, is typically controlled by the cellular content of the most limiting nutrient in accordance with the "cell quota" formulation first proposed by Droop (1968).

An additional feature of phytoplankton nutrient dynamics that can be included in flexible-composition phytoplankton models but not in fixed-composition models is the differential light dependence and day/night timing of photosynthesis and nutrient uptake. Rates of photosynthetic C fixation are tightly controlled by irradiance, specifically by the rate at which photons are absorbed by the photosynthetic light-harvesting pigments. In contrast, NO_3^-, NH_4^+ and $Si(OH)_4$ uptake are less tightly controlled by light. In the ocean, NO_3^- and NH_4^+ are both taken up at night, albeit at rates significantly lower than in daylight (e.g. McCarthy et al., 1996), and nocturnal rates of $Si(OH)_4$ uptake are often indistinguishable from those in daylight (e.g. Nelson and Brzezinski, 1997). This differential timing of uptake is particularly significant from a modeling perspective, especially for the diatoms; K_S values for $Si(OH)_4$ uptake are consistently higher than those for NO_3^- or NH_4^+ uptake, 1–5 μM (see above), as opposed to 0.005–0.5 μM (Harrison et al., 1996). Thus rates of Si uptake are often more severely limited than rates of N uptake under ambient nutrient conditions, especially in HNLC areas (Leynaert et al., 2001; Nelson et al., 2001). However, low instantaneous rates of Si uptake are compensated for to a significant degree by the cells' ability to take up Si throughout the 24 h day/night cycle. Models that shut down diatom Si uptake at night by imposing a fixed Si:C ratio and having photosynthetic C fixation go to zero at night, or through a direct irradiance dependence as with other nutrients, can significantly underestimate the ability of diatoms to grow under in situ conditions.

In addition to including variabible stoichiometric ratios, progress has been made in recent years towards incorporating representations of Fe limitation of diatoms. Several examples exist of models with explicit representations of diatoms with both Si and Fe limitations. For example, Moore et al. (2002a, b) incorporated Fe limitation into their global 1-D, multi-functional group model (discussed in Section 2.1) that includes Fe- and Si-limited diatoms with flexible stoichiometric ratios. Among other things, this model produces realistic global patterns of biogenic silica production (see also Moore et al., 2004, for a 3-D quasi-fixed ratio application of this model). More recently, Jiang and Chai (2004) incorporated the effects of Fe on diatom growth rate and changes of Si:N uptake ratio by diatoms in a paleo-modeling study. They were able to reproduce a high [Fe], low [NO_3^-] condition in the equatorial Pacific during glacial periods, when eolian Fe inputs were presumably higher. Such conditions might have prevented diatoms from out-growing other phytoplankton groups in that system under glacial conditions (Brzezinski et al., 2002). It should be noted, however, that the representation of Fe and Fe–Si interactions in these models is highly simplified compared to the discussion above, especially with respect to Fe dissolution, complexation, bioavailability and scavenging.

2.3.3. Future directions

Substantial progress has been made in developing biogeochemical models with explicit representations of diatoms with Si limitation and cycling. This progress can be attributed in part to the simplicity of the Si cycle relative to other nutrients such as N, P and Fe, but also to the fact that a considerable amount of research has been done over the last 50 years on the Si-uptake kinetics of diatoms, Si thermodynamics and Si variability in situ. There are, however, some important aspects of diatom physiology and silica limitation that have not been widely incorporated into models, such as dark uptake of Si, and there is still much more work to be done in terms of incorporating more realistic Si and Fe limitation interactions and cycling in models. Other biological factors that impact biogenic Si cycling and export, such as diatom species composition, cell morphology and aggregation, also play an important role in determining the Si cycle in the ocean, but their effects are not yet understood well enough to be parameterized well in biogeochemical models.

Another challenge we face at present in modeling the Si cycle is accounting for the impacts of radiolarians and silicoflagellates, which may be particularly relevant for simulating export to the deep ocean. Radiolarians are planktonic protozoa that produce silica skeletons that can range anywhere from tens of microns to millimeters in diameter. Most radiolarians are somewhat spherical, but there exist a wide variety of shapes, including cone-like and tetrahedral forms, and their skeletons tend to have arm-like extensions (spicules) that are used both to increase surface area for buoyancy and to capture prey. Radiolarians include both filter feeders and predators, and they often form symbiotic relations with unicellular algae. They occur in all oceanic regions but are especially common in cold waters, and many are deep-sea

species. Silicoflagellates are small (10–250 μm) golden-brown algae (Chrysophyceae) with silica skeletons composed of a network of bars that resemble those of radiolarians, but these skeletons are generally much less complex. Only a few species of silicoflagellates are known, and these are usually most abundant in colder waters (Lalli and Parsons, 1997).

The silica skeletons of radiolarians and silicoflagellates are preserved in the fossil record and have been widely used in paleo-oceanographic studies. Although seasonal and interannual variations in the abundance of these two groups have been documented in sediment traps (Takahashi, 1997), mass quantitative estimates of their fluxes versus diatoms are difficult to make and are considered unreliable (Archer et al., 1993). Suffice it to say that silicoflagellate skeletons usually comprise a small fraction (less than 1–2%) of the siliceous component of marine sediments, and they are generally much less abundant than diatoms. In contrast, sediments composed almost entirely of the siliceous remains of radiolarians (radiolarian ooze) are observed.

To our knowledge, no large-scale prognostic biogeochemical models have included biogenic silica production specifically associated with silicoflagellates or radiolarians. As with the carbonate-forming forams and pteropods (discussed below), such efforts are inhibited by a general lack of physiological and ecological information for model development and a paucity of quantitative validation data. The omission of these groups—particularly radiolarians—in current models that account for only diatom-associated silica production almost certainly will result in significant underestimation of biogenic silica formation, export and dissolution at some times and places at high latitudes.

2.4. Calcifying autotrophs and heterotrophs

2.4.1. State of our knowledge

Like silica, calcium carbonate (as calcite and aragonite) is another compound with precipitation and dissolution strongly influenced by marine organisms. And also like silica, the basic components of the calcium carbonate cycle can be represented in terms of dissolved, living biogenic and detrital biogenic constituents (Fig. 4). Within the pelagic environment, coccolithophores, planktonic foraminifera and pteropods represent the most important groups of calcifying organisms (Fabry, 1989; Westbroek et al., 1993), and we restrict our

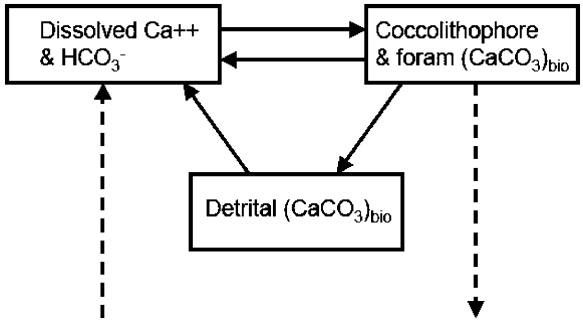

Fig. 4. Essential components of an upper ocean calcium cycle model.

discussion to these groups. The precipitation of calcium carbonate ($CaCO_3$) alters the equilibrium of the inorganic carbon system and alkalinity of seawater through the following calcification (Feely et al., 2004a):

$$Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3 + H_2O + CO_2.$$

This reaction leads to a disequilibrium in the ocean carbonate system that depletes surface CO_3^{2-}, reduces alkalinity and tends to increase pCO_2 (Zeebe and Wolf-Gladrow, 2001). Its impact on pCO_2 has the potential to significantly reduce the CO_2 influx into the surface ocean. On the other hand, the formation and export of $CaCO_3$, also referred to as particulate inorganic carbon (PIC), contributes to the overall biogenic carbon flux to the deep ocean. For these two reasons, the process of calcification (PIC production) is already accounted for in many biogeochemical models (Six and Maier-Reimer, 1996; Moore et al., 2002a, b). Many modeling studies have simply assumed a fixed PIC to POC ratio in organic-matter formation (see discussion below). In addition to the impacts of calcification on alkalinity and PIC export, calcium carbonate can provide ballast that facilitates the export of POC (Armstrong et al., 2002). This "ballast hypothesis" suggests that POC export is more efficient in the presence of ballast materials such as calcite (and also silica) frustules (see Section 3.3 below).

Profiles of the vertical flux of $CaCO_3$ into sediment traps reveal a more-or-less exponential decline with increasing depth below the euphotic zone (Milliman et al., 1999), an observation that implies a net loss of $CaCO_3$ within each depth stratum bounded by a pair of sediment traps. Milliman et al. (1999) have suggested that the inferred dissolution of $CaCO_3$ at depths well above

the chemical lysocline may be due to biological processes. These observations imply that the production of $CaCO_3$, whether by autotrophs or heterotrophs, is closely correlated with sunlight and that below the euphotic zone there is net consumption of $CaCO_3$. Within the euphotic zone, production of $CaCO_3$ by heterotrophic foraminifera and pteropods would cause calcification to be underestimated if based on PIC/POC ratios in strictly photosynthetic organisms. Even if heterotrophic production of $CaCO_3$ is taken into account, variability in the relative abundance of autotrophic and heterotrophic calcifying species (Eguchi et al., 2003; Kuroyanagi and Kawahata, 2004) argues against the use of a single PIC/POC ratio for the oceans. To overcome these problems in models,one must explicitly decouple carbonate production from total photosynthesis and simulate carbonate formation by heterotrophic organisms separately (see below).

Westbroek et al. (1993) and Fabry (1989) stressed that the calcite-producing coccolithophorid *Emiliania huxleyi* should be regarded as a key species for studies on global biogeochemical cycles and climate modeling. The attention paid to this one species must be understood in terms of its potential role in climate: it is an important calcifier in the ocean (Fabry, 1989), and it represents a potentially significant source of dimethyl sulfide (see Section 2.5). But to some degree, the extraordinary attention is also a consequence of our ability to detect *E. huxleyi* using satellites (Fig. 5 and discussion below). As a result, much of what we know about coccolithophorids has been obtained from this cosmopolitan species. Except for polar regions, *E. huxleyi* is ubiquitous in the ocean and has been considered in numerous physiological studies (Paasche, 2001). Although many experiments have focused on *E. huxleyi*, only a few studies provide substantial information that allows for a reasonable implementation of coccolithophorid dynamics into an ecosystem model.

In general, blooms of *E. huxleyi* follow those of diatoms in waters that have been recently depleted in inorganic nutrients and are becoming more stratified (Holligan et al., 1993). The environmental conditions required for the development of these blooms have been proposed and include, either

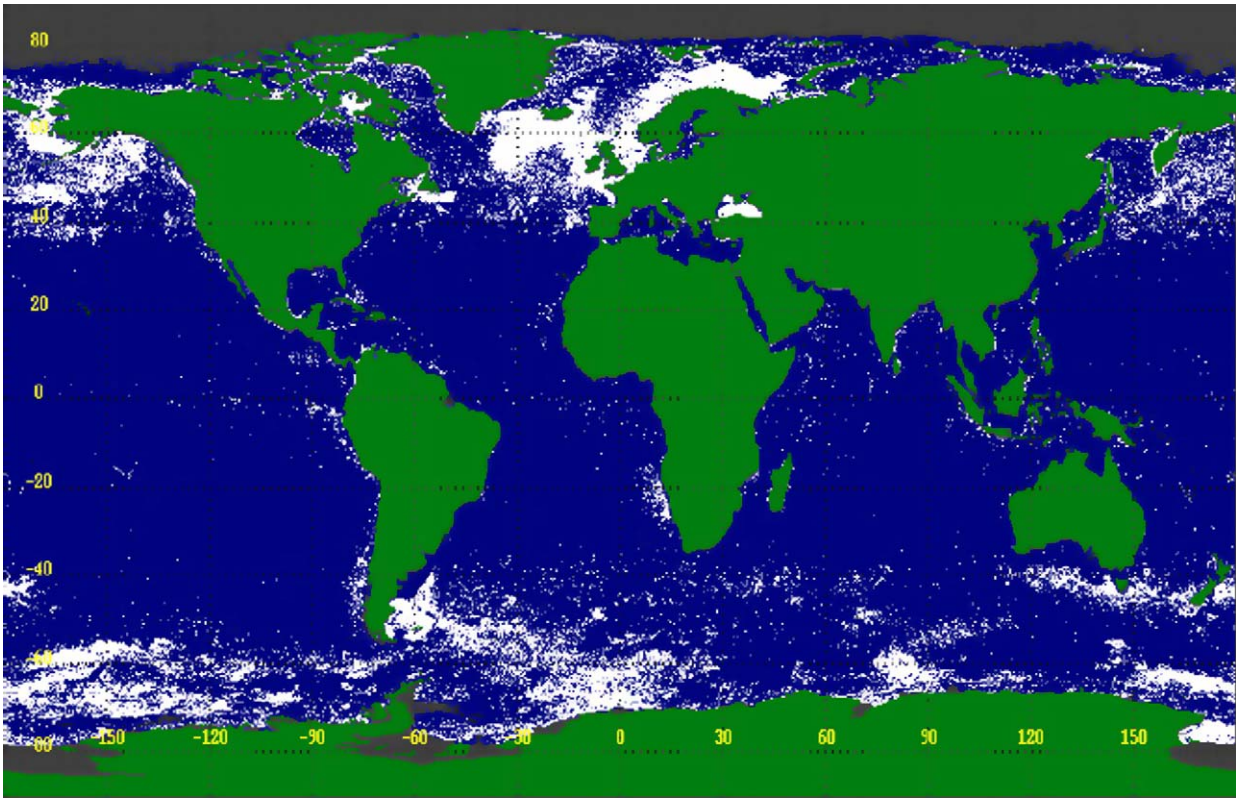

Fig. 5. Composite of classified *Emiliania huxleyi* blooms detected in SeaWiFS imagery from September 1997 to March 2004.

individually or in combination, high incident irradiance (Nanninga and Tyrrell, 1996), low inorganic phosphate concentrations (Egge and Heimdal, 1994; Townsend et al., 1994) and assimilation of dissolved organic phosphate (Aksnes et al., 1994); high N:P ratios (Riegman et al., 1992), low CO_2 concentrations (Nimer et al., 1994) and low microzooplankton grazing (Holligan et al., 1993). *E. huxleyi* effectively acclimatizes to high irradiance due to their resistance to photo-inhibition (Balch et al., 1992; Nanninga and Tyrrell, 1996). Low CO_2 conditions may be favorable for *E. huxleyi* because protons released through the process of calcification ($HCO_3^- + Ca^{2+} \rightarrow CaCO_3 + H^+$) may be used to transform bicarbonate to CO_2 ($HCO_3^- + H^+ \rightarrow CO_2 + H_2O$) which is then used for photosynthesis (Brownlee et al., 1994; Nimer et al., 1994; Brownlee, 1997; Laws et al., 2002).

In the case of ecological interactions controlling heterotrophic calcification, very little is known. What little we do know is mostly restricted to the abundance and dynamics of some specific planktonic foraminifera groups such as *Orbulina universa* and *Globigerina bulloides*, which derives from the fact that the fossil shells of these species have been the focus of numerous paleo-oceanographic studies. For example, the ratio of ^{13}C to ^{12}C measured in the shells is used to reconstruct pCO_2 and marine productivity on geological time scales. The publications of Hemleben et al. (1989) and Wefer and Berger (1991) include a good review of foraminifera, which are unicellular protozoa with calcareaous shells (or ''tests''), the mineral form of the $CaCO_3$ being calcite. They are abundant throughout the entire ocean and inhabit depth strata ranging from surface waters to the deep sea. Foram tests are relatively large and heavy compared to coccoliths. As a result, they sink more rapidly and are therefore more likely to escape dissolution at shallow depths. Sediment-trap studies have shown that calcite fluxes in the deep sea are dominated by foram shells and that sinking rates are very rapid (i.e., hundreds to thousands of meters per day, Honjo et al., 1999). Schiebel (2002) estimates that foraminifera account for 23–56% of the total open marine $CaCO_3$ flux at 100 m and 32–80% of the total deep-marine calcite budget. Thus, it is likely that models that lack this vector for calcite export systematically underestimate PIC fluxes throughout the water column.

Pteropods also produce $CaCO_3$ shells, but the mineral is aragonite, which is about 50% more soluble in seawater than calcite. The shells measure from a few to 30 mm in diameter, and like forams they have been used extensively in paleo-oceanographic studies. Pteropods can be very abundant in the surface ocean, especially in polar seas, and they are all heterotrophic suspension feeders. The shells of these animals sink and accumulate in some regions to form calcareous sediment known as ''pteropod ooze'', which is distributed over a relatively large area of the Atlantic, Mediterranean and northern Indian oceans and is important in adjusting the ocean's alkalinity (Milliman, 1974; Berner, 1977; Betzer et al., 1984b). This would suggest that it may be important to include them in carbon cycle models. Quantifying the contribution of pteropods to carbonate fluxes is confounded by the fact that their shells dissolve rapidly in sediment traps. Dissolution rates are on the order of 4–14% per day (Betzer et al., 1984a). Sediment-trap deployments, which often last a week or more, may therefore greatly underestimate the contribution of pteropod shells to the PIC flux. In parts of the ocean where pteropods are abundant, the contribution of pteropod shells to the export of PIC from the euphotic zone will very likely be important and comparable in magnitude to the flux of foraminifera. However, at depths of several kilometers, the PIC flux is likely to be dominated by coccolithophorids and foraminifera (Honjo, 1996).

2.4.2. State of our models

Calcification has been represented in biogeochemical models in a variety of ways, which range from assuming a fixed ratio of calcification to total photosynthesis (e.g. Paetsch et al., 2002) to explicit, dynamic representations of coccolithophorid growth, calcite production and export (Aksnes et al., 1994; Tyrrell and Taylor, 1995). The obvious advantage of the former is that it allows one to account, at some level, for calcification in an ecosystem model without resolving the abundance and variability of calcifying species. Although it is clearly a gross oversimplification of reality, representing calcification as a simple function or fraction of primary production is supported by the observation that the production of coccoliths in *E. huxleyi*, is a light-dependent process (Paasche, 1964, 2001). Furthermore, a variety of experimental data are available on the carbonate/organic carbon (PIC/POC) ratio (e.g. Nimer and Merrett, 1993; Balch et al., 1996; Buitenhuis et al., 1999). For

photosynthetic calcifying organisms, a PIC/POC ratio of 1 is commonly observed. However, in order to represent calcification in an ecosystem model one must also prescribe the proportion of calcifying to non-calcifying phytoplankton species; for example, an "overall" molar $CaCO_3$:POC ratio of 1/40 has been observed and then applied in an ecosystem model for the European Station for Time-series in the Ocean Canary Islands (ESTOC) by Paetsch et al. (2002).

This fixed PIC/POC approach may inaccurately represent calcification's role in the oceanic carbon cycle because the proportion of calcifying species in the phytoplankton changes dramatically in both time and space, and it does not account for variability in PIC/POC ratios due to changing CO_2 concentrations, as shown for corals (Gattuso et al., 1998; Kleypas et al., 1999; Langdon et al., 2000) and coccolithophores (Riebesell et al., 2000; Zondervan et al., 2002). There is also evidence for decoupling of calcification and photosynthesis in calcifying species, i.e. due to trace metal availability (Schulz et al., 2004), during darkness (van der Wal et al., 1994; Paasche et al., 1996; Paasche, 2001), and under high-light conditions, where light inhibition of calcification has not been observed (Nanninga and Tyrrell, 1996).

The first ecosystem model with an explicit representation of coccolithophores was presented by Aksnes et al. (1994). Their basic approach was to decouple nitrogen from phosphorus availability for algal growth, accounting for a residual source of DOP for growth of *E. huxleyi*. They fitted the model results to match the observations of a mesocosm experiment. In the model study of Tyrrell and Taylor (1995) two-state variables, namely *E. huxleyi* and phosphate, were added to the original nitrogen-based succession model of Taylor et al. (1993), which is applicable for open-ocean simulations. They also adopted the idea of using the DOP pool as an additional source of phosphorus for *E. huxleyi* growth. Both studies support the hypothesis that the high affinity to an extra source of organic phosphorus does allow *E. huxleyi* to succeed under phosphorus stress. High nitrate:phosphate ratios during winter mixing are a good predictor of phosphorus-limited phytoplankton growth during the summer period of maximum solar irradiance. These conditions allow coccolithophores to outcompete other phytoplankton. However, high antecedent nitrate:phosphate ratios are not a necessary condition for *E. huxleyi* blooms. Lessard et al. (2005) show that coccolithophorid blooms develop in many areas where nitrate:phosphate ratios are low. They therefore stress that we need to understand better the utilization of dissolved organic nitrogen (DON) and ammonium by coccolithophores as well.

Iglesias-Rodríguez et al. (2002) employed an empirical approach for describing the environmental conditions favorable to the development of *E. huxleyi* blooms. Because *E. huxleyi* blooms can be detected from space (Holligan et al., 1983; Brown and Yoder, 1994, Fig. 5), it is possible to analyze their distribution pattern and relate it to the coincident physical environment. Based on a comparison between the presence of *E. huxleyi* blooms detected in SeaWiFS ocean-color imagery and contemporaneous key chemical and physical variables, Iglesias-Rodríguez et al. (2002) deduced that large-scale coccolithophorid blooms were located in regions possessing sea-surface temperatures (SST) between 3 and 15 °C, critical irradiance values (defined as the product of the surface irradiance and the ratio of the depth of the euphotic zone to the depth of the mixed layer) between 25 and 150 μmol quanta $m^{-2} s^{-1}$ and decreasing nitrate concentrations ($\Delta N/\Delta t < 0$). Ten environmental variables, including salinity, SST, mixed-layer depth, euphotic zone depth, irradiance, nitrate, phosphate and silicate concentrations, were examined in relation to the classified *E. huxleyi* blooms. These findings were used to construct an empirical probability model that predicts the occurrence of *E. huxleyi* blooms based upon these environmental constraints (Iglesias-Rodríguez et al., 2002). Although their model does not rely on verifiable mechanistic relationships, the results provide valuable information that can be used to parameterize calcification in large-scale simulations or constrain dynamically predicted rates.

We would like to stress that the amount of attention that has been paid to *E. huxleyi* blooms is probably disproportionate to their contribution to global calcification. Though impressive, the blooms of *E. huxleyi* detected in satellite ocean color may play only a minor role in the annual production of calcite on a global scale (Brown and Yoder, 1994; Sarmiento et al., 2002). Based on a simple box model and observations of vertical gradients in potential alkalinity and nitrate, Sarmiento et al. (2002) conclude that the dominant contribution to global calcification comes from "low-latitude non-bloom-forming coccolithophores or other

organisms such as foraminifera and pteropods". As we mentioned above, based on an analysis of multinet and sediment-trap samples, Schiebel (2002) concludes that planktonic foraminifera account for 23–56% of the total open marine $CaCO_3$ flux at a depth of 100 m. The focus of modeling efforts on *E. huxleyi* appears to be largely a consequence of the fact that it is the only pelagic calcifier for which we have global concentration measurements and extensive physiological studies, i.e., we can measure it, so we model it. Explicit representation of the distribution and calcification rate of low-latitude non-bloom-forming coccolithophores and other calcifying groups, such as foraminifera and pteropods (Sarmiento et al., 2002) is limited or lacking in biogeochemical models. This shortcoming must be remedied if we are to adequately model calcification in the pelagic ocean.

It is not straightforward to include foraminifera as a major representative for a single functional group of calcifying heterotrophs in a model because different species function at different trophic levels in marine ecosystems, i.e., some are herbivores and some are carnivores. Furthermore, some have algal symbionts attached to their outer spines (mostly dinoflagellates) and therefore function as part of the autotrophic community as well. To our knowledge, there have not yet been any attempts to specifically account for foram calcification in large-scale, marine ecosystem/biogeochemical models. Rather, modeling efforts with foraminifera that have been carried out to date have focused on the micro-environment of *O. universa* (e.g., Wolf-Gladrow et al., 1999; Zeebe et al., 1999). These studies show that vital effects within the micro-environment of the cells (shell surrounded with symbionts) primarily determine the calcification rate rather than the carbonate chemistry of the surrounding water. Micro-environmental conditions also affect isotopic fractionation. Their findings suggest that, even if we were able to model the seasonal distribution of these symbiotic forams, it would be difficult to derive the correct calcification rates from the water's bulk biochemical conditions or from cellular physiological state. Despite such problems, it may be possible to make some progress if we restrict our initial modeling attempts to non-symbiotic forms, such as *G. bulloides*, which dominate the foraminferal flux to the ocean floor in the eastern North Atlantic (Sautter and Thunell, 1989; Sautter and Sancetta, 1992). Data on abundance, distribution and some dynamical details are provided by Schiebel et al. (1997). Interestingly, their study gives support to the idea that lunar cycles have an influence on the reproductive cycles of forams, which may complicate their consideration in an ecosystem model.

Similarly, we are not aware of any large-scale biogeochemical models that account explicitly for pteropods. As with forams and radiolarians, any efforts to include them in models will be confounded by the fact that we know very little about their physiology, ecology and time/space variability.

2.4.3. Future directions

Although considerable progress has been made in recent years in terms of understanding the factors that control some of the pelagic calcifying groups (i.e., coccolithophorids and specifically *E. huxleyi*), we conclude that current approaches for representing calcification in large-scale biogeochemical models are crude (e.g., specifying calcification as a fixed fraction of organic-matter production) and/or substantially incomplete (i.e., focusing only on *E. huxleyi*). In order to advance the state-of-the-art, we must first improve our ability to measure calcification variability in the ocean and quantify the calcification rates associated with all of the major calcifying groups. Once these data are in hand, we will be in a much better position to develop more complete dynamic models. Then the major challenge will be incorporating these additional groups into models, such as pelagic coccolithophorids that do not form near-surface blooms that are optically distinct, and higher trophic level calcifiers like the foraminifera that contribute substantially to calcite export to the deep ocean and sediments.

2.5. DMS production

2.5.1. State of our knowledge

DMS is the predominant volatile sulfur compound in oceanic surface waters, representing $>90\%$ of the oceanic non-sea salt sulfur flux and $>50\%$ of the global non-anthropogenic sulfur flux (Bates et al., 1992; Chin and Jacob, 1996). Presently, the upper water column is supersaturated when compared to atmospheric DMS and supports a sustained flux to the atmosphere estimated at 15–33 $Tg\,S\,yr^{-1}$ (e.g. Kettle and Andreae, 2000). Once ventilated to the atmospheric marine boundary layer, the chemical degradation products of DMS emissions have the potential to impact global climate through multiple pathways. DMS is

oxidized to a variety of compounds, including sulfate aerosols, which either function as new cloud condensation nuclei (CCN) or promote the growth of existing condensation particles. This results in changes to cloud optical properties and indirectly reduces the amount of incident solar radiation reaching the surface of the ocean, particularly in remote marine regions (Andreae and Crutzen, 1997). The concomitant increase in aerosol loading produces an increase in the backscattering potential of the atmosphere, directly reducing incident solar radiation. By changing the background levels of CCN, natural DMS emissions serve to alter the magnitude of direct and indirect anthropogenic sulfate emission forcing in polluted air masses (e.g. Jones et al., 2001). DMS-derived sulfate aerosols also can alter the acid–base chemistry of the atmosphere and react with rain droplets to produce acid rain. Oceanic DMS emissions have the potential to exert considerable control over planetary albedo and hence climate (Charlson et al., 1987). However, attempts to confirm DMS-aerosol-climate feedbacks have not led to conclusive results or a community consensus.

The concentration of DMS in seawater reflects a complex interplay of physical, chemical and biological processes across a variety of trophic levels (Fig. 6). DMS and an acrylic acid by-product are derived from bacterial- and phytoplankton-mediated enzymatic cleavage of dimethylsulfoniopropionate (DMSP). Intracellular concentrations of DMSP vary between different phytoplankton species by five orders of magnitude (Keller, 1989; Andreae and Crutzen, 1997), with the highest consistent DMSP synthesis rates observed for dinoflagellates and prymnesiophytes (including coccolithophores and *Phaeocystis*). The physiological role for DMSP remains unclear. Suggested roles vary widely (Simó et al., 2002) and include osmotic regulation, chemical defense against grazers, cryoprotection and most recently, an internal antioxidant regulation system (Sunda et al., 2002). Some DMS is excreted directly from algae, with the physiological state of the algae and the degree of environmental stress influencing the rate of emission. DMS is also produced through bacterial transformation of extracellular DMSP that has entered the water column via cell lysis (Kiene, 1990; Kiene and Service, 1991; Ledyard and Dacey, 1994) and zooplankton grazing (Dacey and Wakeham, 1986; Nguyen et al., 1988; Belviso et al., 1990). DMS is lost from the water column through

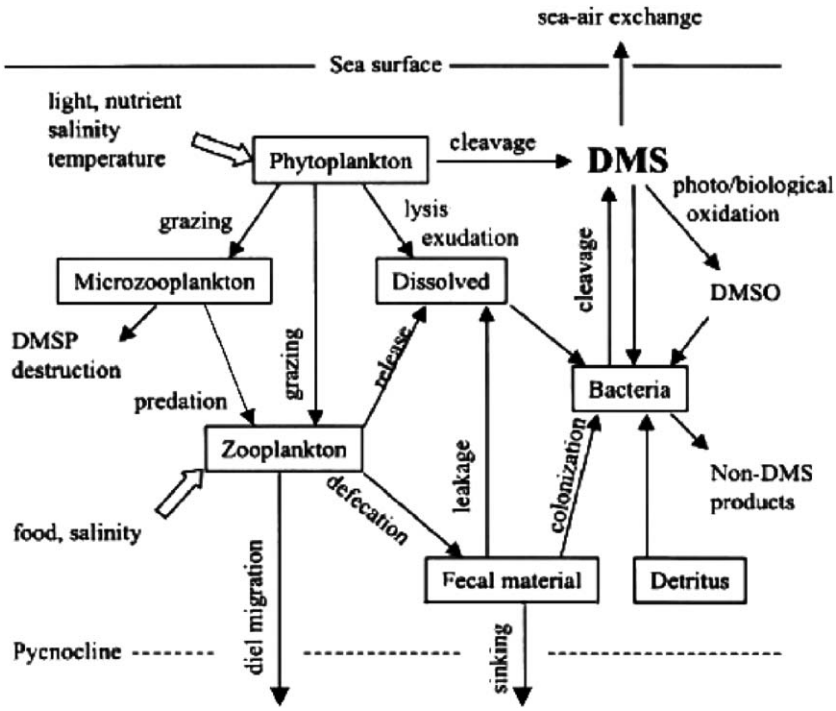

Fig. 6. Schematic box diagram of DMSP dynamics in the pelagic food web. Open arrows represent known factors that affect DMSP pools, thin arrows flux between pools. Modified and reprinted with permission from Tang et al. (2000). ©2000, Inter-Research.

heterotrophic bacterial consumption, photolysis, adsorption onto sinking particles, mixing below the thermocline and ventilation to the atmosphere (see Simó, 2001 for a review).

2.5.2. State of our models

A variety of efforts are ongoing to develop seasonally and spatially resolved global models to identify the principal processes controlling the concentration of DMS in seawater. Recent studies have developed predictive relationships for modeling oceanic surface DMS inventories based primarily on empirical formulations. These models are parameterized in terms of regressions formulated from the ratio of SeaWiFS-derived surface chlorophyll to Levitus mixed-layer depth (Simó and Dachs, 2002), a semi-empirical relationship for community structure as a function of SeaWiFS-derived chlorophyll concentration (Aumont et al., 2002; Belviso et al., 2004b), or as the product of SeaWiFS-derived chlorophyll and climatological nutrients and mean daily shortwave radiation (Anderson et al., 2001). While these models all demonstrate varying degrees of success in certain geographic regions, a review by Belviso et al. (2004a) indicates extremely weak correlations between modeled and measured DMS concentrations in all cases. What is striking is that the iterative interpolation schemes presented in Kettle et al. (1999) and Kettle and Andreae (2000) also produce low correlations between DMS observations and interpolated DMS due to the sparseness of measurements. The empirical DMS models show considerable disagreement at subtropical latitudes (20–40°) and the poles with respect to the magnitude and existence of seasonal variability. This is critical as estimates suggest that subtropical oligotrophic gyres alone account for $>50\%$ of the global oceanic DMS flux (Kettle and Andreae, 2000). All in all, the results from the suite of empirical surface DMS models differ markedly and do not reach a consensus on the global spatial or temporal distribution of DMS. Furthermore, because the model formulations differ widely, it is unclear if they will diverge or converge under changing environmental conditions.

Several prognostic biogeochemical models have been developed that include explicit dynamic representations of DMSP and DMS concentrations and their production and cycling in a pelagic ecosystem (e.g. Gabric et al., 1993, 2003; Archer et al., 2002; Lefèvre et al., 2002; Cropp et al., 2004; Le Clainche et al., 2004). These models vary widely in their linkages to the carbon or nitrogen based ecosystem models that they are embedded in and in the number of phytoplankton (1–3), zooplankton (1–3) and bacterial (0–2) compartments simulated. They also vary in terms of how DMSP and DMS production is linked to phytoplankton production and food web interactions. Comparisons of the results of these models with estimated and observed DMS distributions suggest that while they seem to represent the interaction between the biological and physical processes reasonably well on local scales, they contain a host of poorly constrained parameters (Vézina, 2004). One of the major difficulties in validating the parameter values in vertically resolved DMS models is that the only widely available, vertically resolved DMS and DMSP dataset is the Dacey et al. (1998) 1992–1994 time-series at the Bermuda Atlantic Time-series Study (BATS) station. There are no widely distributed independent subsurface datasets for model validation. In addition, available fully mechanistic DMS models often contain rate constants optimized to describe a specific short-term event such as a phytoplankton bloom or a Lagrangian experiment (e.g., Gabric et al., 1993; Watts and Bigg, 2001), or are regional in scope (e.g., the Southern Ocean, Gabric et al., 1998) making their extrapolation to global scales questionable (Vézina, 2004).

Additionally, many current models do not directly incorporate emerging evidence from modeling and field campaigns, which indicate that oceanic DMS and DMSP dynamics are strongly regulated by physical and chemical factors (e.g. Toole and Siegel, 2004). DMSP and its oxidation products (including DMS) have been shown to be highly effective scavengers of reactive oxygen species created during normal photosynthetic processes. The Sunda et al. (2002) antioxidant hypothesis suggests that phytoplankton synthesize DMSP, which is converted intracellularly to DMS, as a method to cope with high levels of oxidative stress resulting from high ultraviolet (UV) light exposure, metal toxicity or low nutrient concentrations. While certain functional groups of phytoplankton are predisposed to have high DMS and DMSP concentrations, Sunda et al. (2002) demonstrated that under conditions of stress, DMS levels in these species can increase 40-fold. Supporting this, Toole and Siegel (2004) demonstrate that $>77\%$ of the variability in mixed-layer DMS concentrations at the BATS site can be explained in terms of daily UV

radiation dose. UV radiation also can inhibit substantially biological DMS and DMSP consumption (e.g., Slezak et al., 2001; Slezak and Herndl, 2003), and DMS photochemical loss is directly proportional to UV irradiance (e.g., Toole et al., 2003). As such, to assess how upper-ocean sulfur cycling will respond to global change, model formulations need to incorporate dynamic DMS and DMSP intracellular concentrations and bulk-rate processes that change in response to the modulating physical environment.

Biogeochemical models with dynamic representations of DMSP and DMS production also have been applied in large-scale modeling efforts to assess climate change scenarios (e.g., Bopp et al., 2003,2004; Gabric et al., 2003, 2004). For example, Gabric et al. (2003) simulated the change in DMS flux in the Eastern Antarctic Ocean (60–65°S, 125–140°E) from 1960 to 2086, corresponding to equivalent CO_2 tripling relative to pre-industrial levels. This was accomplished by forcing the Gabric et al. (1993) DMS model, which incorporates three biotic state variables (heterotrophs, autotrophs and zooplankton) with output from a coupled atmospheric-ocean GCM. Their results indicate that by 2086 the annual integrated DMS flux in the Eastern Antarctic Ocean will increase by 20% in ice-free waters, with a greater increase of 45% in the seasonal ice zone. Gabric et al. (2004) carried out a similar modeling study utilizing the empirical relationship between DMS and the ratio of SeaWiFS chlorophyll to Levitus mixed-layer depth, developed by Simó and Dachs (2002), and observed increases in DMS flux of 107% for 50–60°S, 46% for 60–70°S and $<10\%$ for the tropics. In contrast, Bopp et al. (2003), utilizing the empirical community structure index of Aumont et al. (2002), estimates a reduction of DMS fluxes by as large as 60% in the tropical Pacific. While all climate change scenario simulations agree that DMS flux changes will be characterized by large spatial heterogeneities, the magnitude of these changes is strongly dependent on the model formulation chosen and varies widely.

2.5.3. *Future directions*

Although progress has been made over the last decade in efforts to simulate DMS distributions, modeling of the contemporary DMS biogeochemical cycling is still in its infancy, and many significant problems remain. One of the most obvious issues is the lack of understanding of the physiological and functional dependencies of DMS and DMSP. Without understanding why phytoplanktons synthesize DMS and DMSP, it is unlikely that models will be able to capture anything beyond large-scale DMS distributions. Additionally, current empirical formulations shed little light on how DMS biogeochemical cycling processes will be altered in response to changing environmental and ecosystem structure conditions. Future endeavors to improve estimates of DMS flux based on traditional observational approaches should focus on deriving more accurate estimates of DMS rate processes and their functional dependencies. In addition, models should continue to incorporate emerging evidence, such as the importance of vertical mixing and UV radiation exposure. There is a need for process-oriented studies, combined with the application of biotic models, to improve our understanding of the processes that control the production and cycling of DMSP and DMS in seawater and air. Efforts should continue to compile databases from different oceanic regions and seasons containing information on particulate and dissolved DMSP concentrations and atmospheric and seawater concentrations of DMS, in conjunction with relevant environmental, biological and ancillary variables. This information will assist in elucidating cycling mechanisms for DMS to improve regional and temporal characterizations of seawater and atmospheric DMS concentrations, and thus DMS sea-to-air flux.

3. Modeling and understanding functional groups in the Ocean

In the section we address several different subjects, questions and problems that are relevant to functional group modeling. We begin with a look at the paleo-oceanographic record to see what it reveals about how functional group diversity and the relative abundance of some key organisms have changed in the past (Section 3.1), and a review of what chemical fields in the ocean can tell us about functional group activity (Section 3.2). Then we embark upon discussions focusing on the crucial role of functional groups and particularly higher trophic levels in modulating export (Section 3.3) and ecosystem structure (Section 3.4). This is followed by a review of the long-standing debate of whether or not we need to include DOM and bacteria explicitly in biogeochemical models (Section 3.5). We then conclude this section with a brief discussion of some new inverse and data assimilation methods that have been recently

applied to help advance the state-of-the-art in biogeochemical modeling (Sections 3.6 and 3.7).

3.1. The paleo-oceanographic perspective

How have functional group diversity and relative abundance changed in the past and why? what can this tell us about what might happen in the future?

The functional groups of phytoplankton in the contemporary ocean reflect the effect of evolutionary forces and changes in climate over more than 3 billion years of Earth history. The most important abiotic driving forces have been changes in the redox state of the ocean and the supply of nutrients as influenced by ocean circulation and continental weathering processes. The impact of these abiotic factors has been modulated by biological responses that, through feedback mechanisms, have modified the climate of the Earth and the oceanic environment, sometimes in very significant ways. The geological record indicates that the first photosynthetic organisms were prokaryotic cyanobacteria. Chemical evidence from Archean shales suggests that photosynthetic organisms were present in the ocean 2.7 billion years ago (Ga) if not earlier (Knoll, 1992, 2003; Brocks et al., 1999). The ocean at that time was anoxic, but the production of oxygen by these organisms radically altered the chemistry of the ocean and atmosphere over the course of the next several hundred million years. With the oxidation of the atmosphere and surface waters of the ocean by roughly 2.4 Ga, evolutionary forces changed dramatically. Dissolved iron and manganese, which would have been abundant relative to the needs of photoautotrophs under anoxic conditions, became scarce in surface waters under oxidizing conditions. In contrast, copper and molybdenum, which would have been scarce under anoxic conditions, became relatively plentiful in the presence of oxygen. Although surface waters became oxic, subsurface waters remained anoxic or hypoxic for a much longer period of time (Kasting, 1993).

Eukaryotic phytoplankton seem to have evolved in the Paleo-proterozoic Era (2500–1600 Ma), presumably the result of engulfment of a coccoid cyanobacterium by a heterotrophic host cell that already contained a mitochondrion (Knoll, 1992), but the rise of modern eukaryotic photoautotrophs began in the Middle Traissic (248–206 Ma). An early schism in eukaryotic phytoplankton resulted in two distinct lineages, the "green" and the "red" (Falkowski et al., 2004). Both utilize chlorophyll *a* as the primary photosynthetic pigment, but they differ with respect to their accessory pigments. Of the major eukaryotic phytoplankton taxa in the contemporary ocean, all but the *Prasinophyceae* belong to the red lineage, whereas virtually all terrestrial algae and plants belong to the green lineage. The decline of the green lineage and the emergence of the dominant red lineage among marine eukaryotic phytoplankton broadly coincide with the oxidation of the ocean during the Mesozoic Era (248–65 Ma) and the associated changes in trace metal availability (Falkowski et al., 2004).

3.1.1. Dinoflagellates, coccolithophores and diatoms

Among the red-lineage taxa, dinoflagellates and coccolithophores flourished during the Mesozoic Era, but have been more-or-less in decline during the Cenozoic (Fig. 7). Red-lineage marine photoautotrophs are now dominated by diatoms, which account for roughly 40% of net primary production and 50% or more of the organic carbon exported to the ocean interior (Smetacek, 1999). What is the explanation for the radiation of dinoflagellates and coccolithophores during the Mesozoic and the hegemony of diatoms in the contemporary ocean?

The Mesozoic Era was a relatively warm period of Earth's history, with weak latitudinal thermal gradients. Globally averaged wind speeds and ocean thermohaline circulation were probably sluggish (Huber et al., 1995). Under these conditions, it is reasonable to assume that the surface waters of the ocean were physically stable and chemically oligotrophic. Mixotrophy, the ability of an organism to function in both an autotrophic and heterotrophic mode, is a lifestyle by no means unique to dinoflagellates, but as a class of algae they exploit this mode of nutrition more than any other (Stoecker, 1999). Mixotrophy may be a particularly effective lifestyle in oligotrophic habitats, where organic nutrients are relatively abundant compared to their inorganic counterparts (e.g., Stickney et al., 1999). It is also an effective mode of nutrition in coastal regions enriched with organic matter derived from land runoff. The warm conditions that prevailed during the Mesozoic precluded large amounts of water being locked up in polar icecaps. Sea level was therefore relatively high, and the ocean flooded many coastal areas. The generally oligotrophic condition of the open ocean and the extensive areas of flooded continental shelves therefore favored mixotrophic algae. Coccolithophores

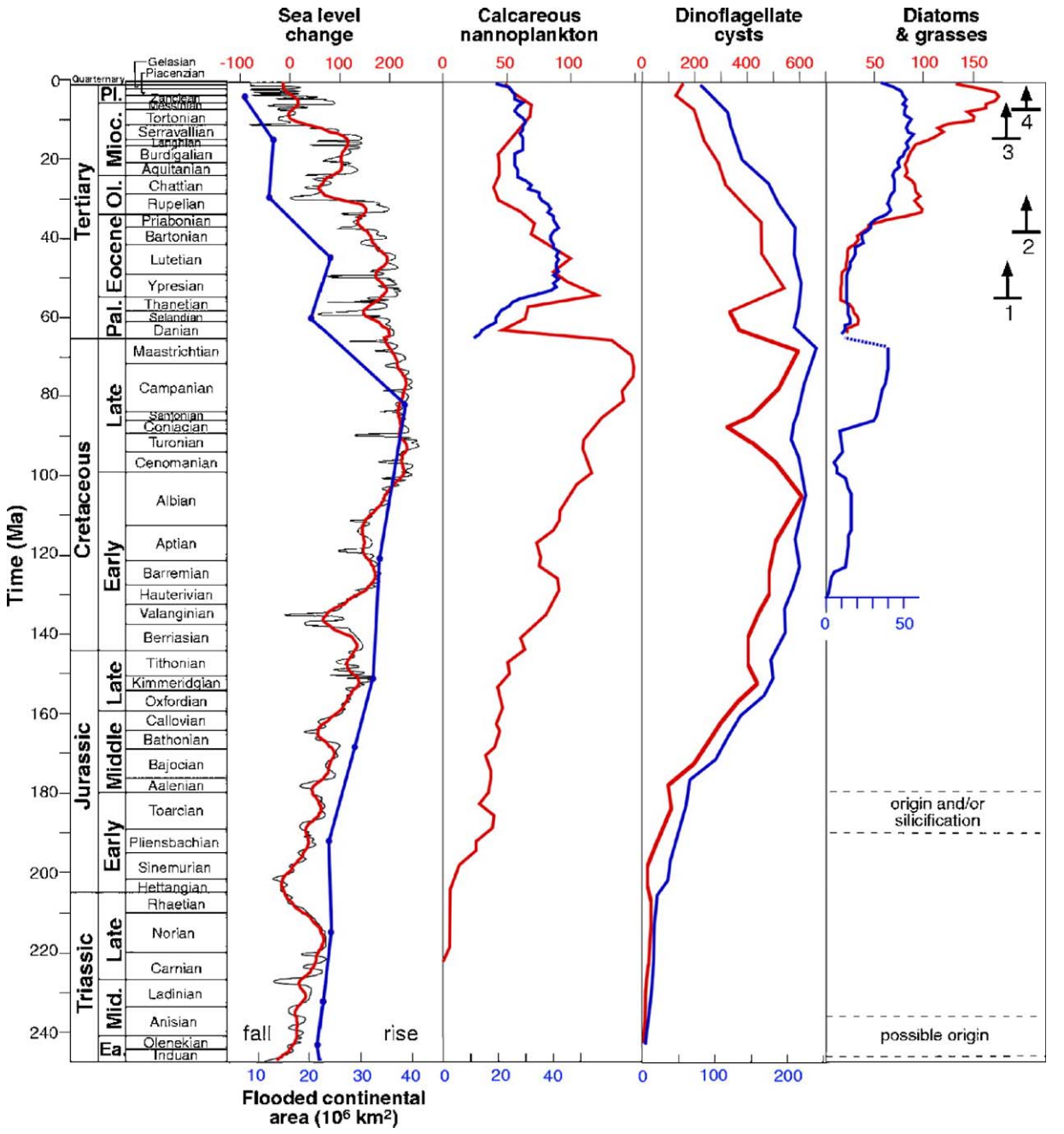

Fig. 7. Geologic time-series showing changes in calcareous nanoplankton, dinoflagellate cysts, diatoms and grasses relative to sea level change from the beginning of the Mesozoic Era to the present. From Falkowski et al. (2004), ©2004, Scientia Marina, reproduced by permission of Scientia Marina. Reprinted with permission from Falkowski et al. (2004). ©2004, AAAS.

are obligate photoautotrophs, but available physiological data indicate that they have a high affinity for inorganic nitrogen and phosphorus. They are therefore well suited to compete with other photoautotrophs in oligotrophic habitats. (It should be noted that small cell size confers a general advantage in nutrient uptake at low concentrations. We would therefore also expect even greater extent/predominance of picoeukaryotic groups, such as the prochlorophytes and *Synechococcus* in the Mesozoic along with the coccolithophores and dinoflagellates.)

During the Cenozoic (65 Ma to present, Fig. 7), several factors altered the balance of competition in favor of diatoms. First, with the development of polar icecaps toward the end of the Eocene Epoch, wind speeds and thermohaline circulation became more vigorous, and upper ocean wind and surface cooling-induced mixing increased (Chandler et al., 1992; Barron et al., 1995). Sea level began a long-term fall that reduced the extent of shallow coastal seas (Fig. 7). Diatoms are well suited to compete with other algae under these conditions, i.e., they are adapted for rapid nutrient uptake in variable conditions and their vacuoles allow them to store nutrients for subsequent growth. Diatoms are therefore able to grow rapidly when nutrients are supplied in an irregular manner (Cullen and MacIntyre, 1998; Strzepek and Harrison, 2004). (See also Tozzi et al., 2004, for an in-depth model-based analysis focusing on the impact of turbulence on the success of diatoms versus coccolithophorids, and how this relates to the relative dominance of these two groups in the geologic past.)

As discussed above, diatoms have an absolute requirement for silicate in order to produce their silica frustules. The principal supply of silicate to the ocean is usually considered to be the weathering of continental rocks. There is reason to believe that the silicate weathering cycle has been gradually increasing during the Cenozoic as a result of changes in continental elevation (Huh and Edmond, 1999). However, these changes cannot explain the sharp increase in diatoms at the Eocene/Oligocene boundary (33.7 Ma). Falkowski et al. (2004) have suggested that the increase may be related to biologically catalyzed silicate weathering and runoff associated with the radiation of silica-rich terrestrial grasses, and further that the stimulation of export production by diatoms may have created a positive feedback loop, with the associated drawdown of CO_2 reducing global temperatures and making the ocean more turbulent, i.e., reduced stratification and increased buoyancy mixing.

3.1.2. *Key N-cycle functional groups*

Biological N_2 fixation evolved very early in Earth history, long before oxygenic photosynthesis (>2.7 Ga). It is a strictly anaerobic process (Postgate, 1987), and the sequence of genes encoding the catalytic subunits for nitrogenase is highly conserved in cyanobacteria and other eubacteria, strongly suggesting an ancient, common ancestral origin (Zehr et al., 1995). Fixed inorganic nitrogen in the archean and early Protozeroic (2500–543 Ma) oceans was scarce before the evolution of diazotrophic organisms (Falkowski, 1997), a condition that would have provided strong evolutionary selection for N_2 fixation. In contrast, soluble reactive phosphorus in archean oceans was probably relatively abundant in the mildly reducing environment of the time (Holland, 1984; van Cappellen and Ingall, 1996). Thus, the archean ocean probably had a very low reactive N:P ratio in the dissolved inorganic phase. As N_2 fixation proceeded, that ratio would have increased with a build-up of ammonium in the ocean interior. The formation of nitrate from ammonium (nitrification) is sequentially catalyzed through a nitrite intermediate by two groups of aerobic bacteria: one group oxidizes ammonium to nitrite, the second oxidizes nitrite to nitrate. Both processes require molecular oxygen; hence, nitrification must have evolved after the introduction of free O_2 in the oceans by oxygenic photoautotrophs (i.e. <2.4 Ga).

The iron required for diazotrophic growth (relative to C, N and P) is substantially higher than that with fixed nitrogen (Kustka et al., 2002). As discussed above, the photosynthetic production of oxygen by cyanobacteria resulted in a dramatic change in the availability of trace metals in the ocean, leaving much of the upper ocean with relatively low inventories of bioavailable iron (Holland, 1984), a condition that has persisted to the present day. The loss of bioavailable iron seems to have been associated with an evolutionary divergence of cyanobacteria and the radiation of new marine species that were capable of nitrogen fixation (Falkowski and Raven, 1997). In the modern ocean, eolian transport of continentally derived dust is a significant, if not the most important, source of iron to the central ocean basins (Duce and Tindale, 1991). In regions far removed from these fluxes, such as the South Pacific, rates of N_2 fixation appear to be low, whereas in areas with higher fluxes, such as the North Atlantic, the rates are higher (Carpenter, 1983; Letelier and Karl, 1996; Gruber and Sarmiento, 1997).

Thus, through the modulation of iron availability, it appears that oxygen also has played an important role in directing the evolution of cyanobacteria and controlling rates of N_2 fixation and the nitrogen inventory of the oceans. However, we reiterate that turbulence and mixing also have a strong impact on the success of diazotrophs, i.e.,

they require warm, stratified, nutrient-depleted conditions for growth due to the high energy requirement of N_2 fixation. Thus, it is likely that changes during the Cenozoic (65 Ma to present, Fig. 7) that altered the balance of competition in favor of diatoms (higher wind speeds, more vigorous thermohaline circulation and increased upper ocean turbulence) would have reduced the success of diazotrophic species.

In the sequence of the three major biological processes that comprise the nitrogen cycle, denitrification was probably the last to emerge (Falkowski, 1997). As discussed in Section 2.2 above, this process (which permits the reduction of NO_3^- to, ultimately, N_2) occurs only in low oxygen environments, i.e., in the modern ocean in continental margin sediments, areas of restricted circulation such as fjords and in open-ocean oxygen minimimum zones (Codispoti and Christensen, 1985; Christensen et al., 1987; Seitzinger, 1988; Devol, 1991). In contrast to nitrogen fixation, denitrification seems to have evolved independently several times; the organisms and enzymes responsible for the pathway are highly diverse, and the pathway is found in both Arachaebacteria and Eubacteria (Zumpft, 1992). With the emergence of dentrification, a circuit for nitrogen was established between the atmosphere and ocean, where N_2 fixation provides a source of nitrogen for photoautotrophic production, but simultaneously, fixed nitrogen is removed from the oceans as N_2.

3.1.3. *What can this tell us about what might happen in the future?*

Clearly, changes in oxygen concentrations have played a central role in the evolution and emergence of many of the key functional groups that influence biogeochemical cycles in the present-day ocean, both directly and also indirectly by influencing the availability of trace metals, particularly iron. Changes in silicate supply also may have been important in modulating shifts in phytoplankton species composition, with increases favoring diatom growth. In general, it appears that climatic shifts that have led to more stratified ocean conditions have tended to increase the prevalence of coccolithophorids, dinoflagellates and diazotrophic species to the detriment of diatoms and vice versa.

The Third IPCC Scientific Assessment (IPCC, 2001) predicts that global warming will lead to generally warmer, wetter and more variable surface ocean conditions from mid- to high latitudes and more El Niño-like conditions in the tropics. The latter implies warming in the tropics, an eastward shift of precipitation, and a reduction in nutrient inputs from equatorial and coastal upwelling. Most models show increased stratification and consequent weakening of the ocean thermohaline circulation, which leads to a reduction of the heat transport into high latitudes of the Northern Hemisphere. These changes, though potentially profound, are not likely to have a large impact on oxygen concentrations and the redox potential of the ocean over the next century. Based upon these considerations alone, we speculate that global warming over the coming decades will give rise to increased dominance by coccolithophorids, dinoflagellates and diazotrophs and lower abundance of diatoms due to increasing stratification (Boyd and Doney, 2002). However, other factors, such as decreases in ocean pH (Kleypas et al., 1999; Wolf-Gladrow et al., 1999; Caldeira and Wickett, 2003; Feely et al., 2004a) and atmospheric iron supply (Mahowald and Luo, 2003) could adversely affect both coccolithophorids (Riebesell et al., 2000) and diazotrophs, respectively.

3.2. *Using chemical fields to diagnose functional group activity*

What can the distributions of nutrients and chemical properties in the ocean tell us about the distributions of functional group activity?

Biological processes have had a profound impact on the distribution of chemical properties in the ocean and, as we have seen, they have directed the evolution of plankton over geologic time. In addition to their long-term consequences, biological processes control variability in chemical properties on much shorter time scales (i.e., days, weeks, seasons and years). In this section, we discuss how these short-term changes in the chemical properties of the ocean (in both space and time) have been used to infer biogeochemical rates and functional group activity in the present-day ocean, and the derived rates that can be used to validate large-scale biogeochemical models.

3.2.1. *Organic carbon net community productivity*

We did not discuss carbon fixation and respiration as distinct biogeochemical functional groups in Section 2 above, in part because these fundamental processes are considered (simulated) by virtually all prognostic biogeochemical models. We must keep in mind, however, that these reactions are extremely

important, i.e., they control the carbon, oxygen and nutrient concentrations in the ocean and therefore must be constrained in models. In fact, changes in the concentrations of these constituents can be used to estimate production and export of organic matter in the euphotic zone. Because biological processes in the ocean are largely seasonal, particularly in extratropical waters, a pronounced annual cycle in "nutrients" (e.g., inorganic C, N, P, Si and O_2) is often observed. In particular, nutrients are removed and oxygen is produced in surface waters by biological activity during summer when light availability is high and the reverse happens during winter when vertical physical exchange dominates (e.g., Takahashi et al., 1993). When these changes are tracked over a seasonal cycle they provide a spatially and temporally integrated estimate of net community production (NCP) (sensu Williams, 1993, i.e., referring to the net balance between autotrophic and heterotrophic processes in the plankton community) and/or potential export production that can be extrapolated over local to global spatial scales. Such integration and extrapolation are difficult to do with in vitro ^{14}C-based primary-production estimates or sediment-trap estimates of export productivity. Chemically derived NCP estimates can therefore provide validation information for large-scale biogeochemical models over temporal and spatial scales that cannot be obtained from direct measurements (Jenkins and Goldman, 1985).

However, estimating NCP from in situ chemical fields has limitations in scope and applicability. Mass balance is required, which necessitates that fluxes (e.g., air–sea exchange, diffusion and entrainment) be well constrained. As a result, accurate estimates of NCP are sometimes difficult to obtain in advectively dominated oceanic systems (Louanchi and Najjar, 2000). Also, although this aproach allows rates of NCP or export productivity to be estimated, it does not provide specific information about the functional groups responsible, unless accompanied by biological information (e.g., pigments, PB and taxonomy, etc.). At present, most studies consist of seasonal to annual estimates of NCP based on climatological data. However, improving datasets will allow interannual variability of NCP to be assessed in the future.

Early studies of NCP using chemical fields focused primarily on local to regional scales, for example, in the polar/subpolar seas (Codispoti et al., 1982, 1986; Jennings et al., 1984; Chipman et al., 1993; Hansell et al., 1993) and subtropical/tropical oceans (Bates et al., 1996b; Emerson et al., 1997). In the last decade, the collection of large global datasets under the auspices of the WOCE/JGOFS programs and climatological datasets (Levitus and Boyer, 1994a, b; Levitus et al., 1994; Bates et al., 1996b; Emerson et al., 1997) has provided estimates of net community production at global and regional scales (e.g. Louanchi and Najjar, 2000; Najjar and Keeling, 2000; Lee, 2001; Gruber and Sarmiento, 2002; Lee et al., 2002; Bates et al., 2006a,b; Bates and Hansell, 2004).

For the global ocean, estimates for NCP have been determined, ranging from ~4.3 to $10.8 \times 10^{15}\,g\,C\,yr^{-1}$ (Table 1). Higher rates of NCP were estimated using seasonal DIC (Lee, 2001; $9.1 \pm 2.7\,Pg\,C\,yr^{-1}$), nitrate changes (Lee, 2001; $10.8 \pm 2.7\,Pg\,C\,yr^{-1}$) and net efflux of biologically produced O_2 (Louanchi and Najjar, 2000, $9.4 \pm 2.7\,Pg\,C\,yr^{-1}$). These estimates were somewhat higher than similar estimates based on the seasonal drawdown of nitrate and phosphate, and dissolved oxygen coupled with C:N:P:O_2 elemental ratio conversions (4.6 and $5.3\,Pg\,C\,yr^{-1}$, respectively; Louanchi and Najjar, 2000). Nonetheless, it appears that the present-day global NCP rate is reasonably well constrained, varying by only about a factor of two.

Similar approaches have been used to estimate NCP for specific ocean basins such as the Atlantic (Lee et al., 2003), Indian (Bates et al., 2006b) and Pacific oceans (Emerson et al., 1997; Bates et al., 2006c). Direct comparisons with estimates of NCP determined from changes in dissolved oxygen, and inorganic nutrients have been obtained for all major ocean basins (Table 1). In addition, other approaches have utilized inverse models with global datasets (Schlitzer, 2004) or datasets coupled with prognostic models (Feely et al., 2004b) to provide additional regional and global constraints on net community production. Rates of organic carbon remineralization in the water column also have been quantified by using in situ changes in chemical fields such as dissolved oxygen (Shulenberger and Reid, 1981; Emerson et al., 2001, 2004; Louanchi and Najjar, 2001) and DIC (Ono et al., 2001).

The global and regional datasets upon which these NCP estimates are based are being continually expanded and improved through on-going programs and survey cruises (e.g. WOCE). In combination with improved boundary fluxes, we can expect that the uncertainties in NCP estimates will progressively decline in the coming years.

3.2.2. $CaCO_3$ production and dissolution

Similar mass balance approaches have been used to estimate the NCP of $CaCO_3$ on regional and global scales. On the global scale, Lee (2001) also used the WOCE/JFOFS global CO_2 dataset to derive a set of salinity-normalized total alkalinity-SST relationships for the global oceans, which were then combined with seasonal temperature distributions to obtain a global annual estimate of 1.1 ± 0.3 Pg C as $CaCO_3$ particles in the oceans. This approach has been coupled with studies of the changes in total alkalinity distributions in the deeper parts of the water column (Feely et al., 2004a) to develop a better understanding of the total budget of $CaCO_3$ particles in the oceans from production in the euphotic zone to dissolution in intermediate and deepwater depths. Feely et al. (2004a) estimate, for example, that approximately 45–65% of new production of $CaCO_3$ is dissolved in the water column, with the majority of the dissolution occurring in the upper 2000 m. On the local scale, non-conservative changes in alkalinity–salinity relationships have been shown to be indicative of $CaCO_3$ production due to coccolithophore calcification (Purdie and Finch, 1994; Robertson et al., 1994; Bates et al., 1996a). However, this approach has not yielded quantifiable rates of calcification for specific calcifying organisms. Consequently, researchers have determined shell growth rates for selected groups of organisms (e.g. pteropods and heteropods) using ^{45}Ca uptake studies (Fabry, 1989, 1990). While these approaches are very useful for estimating the relative importance of selected groups of organisms to the total $CaCO_3$ budget in surface waters, they are labor intensive and require specialized procedures employing radioactive isotopes.

3.2.3. Nitrogen fixation and denitrification estimates

The oceanic nitrogen budget is dynamic and set by the balance of sources and sinks of nitrogen. As discussed above, fixed nitrogen is lost from the oceans during the process of denitrification, while new nitrogen sources to the ocean include: wet and dry deposition of nitrogen from the atmosphere; riverine inputs of inorganic and organic N, and N_2 fixation by marine diazotrophs. Geochemical estimates of nitrogen fixation are based on quantification of excess nitrate relative to phosphorus in the thermocline compared to the global mean N/P (i.e. N/P of 16:1, Redfield et al., 1963; Takahashi et al., 1985; Anderson and Sarmiento, 1994).

Anomalous N/P ratios in the North Atlantic Ocean were recognized and assigned to nitrogen fixation by Fanning (1987, 1992). More recently, the tracers N^* (Michaels et al., 1996; Gruber and Sarmiento, 1997) and DIN_{xs} (Bates and Hansell, 2004; Hansell et al., 2004) have been introduced to

Table 1
Global and regional annual estimates of net community production (NCP)

Method	Annual NCP (10^{15} g C yr^{-1})	Reference
Global		
CO_2 mass balance	9.1 ± 2.7	Lee (2001)
Oxygen mass balance	9.4	Louanchi and Najjar (2000)
Oxygen mass balance	4.5–5.6	Najjar and Keeling (2000)
Inorganic nutrient mass balance	4.6–5.3	Louanchi and Najjar (2000)
Inorganic nutrient mass balance	10.8 ± 2.7	Lee (2001)
Pacific Ocean		
Organic carbon remineralization	5.3 ± 1.0	Feely et al. (2004b)
Inverse Model	5.0	Schlitzer (2004)
Indian Ocean		
CO_2 mass balance	0.84–1.32	Bates and Hansell (2004)
Oxygen mass balance	1.1	Louanchi and Najjar (2000)
Ocean circulation model (high vertical diffusivity)	1.5–1.8	Gnanadesikan et al. (2002)
Ocean circulation model (low vertical diffusivity)	1.1–1.6	Gnanadesikan et al. (2002)
Atlantic Ocean		
Oxygen and nutrient mass balance	1.3	Louanchi and Najjar (2001)

The units are given in 10^{15} g C yr^{-1}(Pg C yr^{-1}). Annual NCP rates were estimated from CO_2, oxygen, inorganic nutrient mass balance approaches, ocean and ocean productivity synthesis models and coupled ocean biological–physical models.

indicate the degree of nitrate enrichment. The tracer N^* is defined as

$$N^* = (N - 16P + 2.90) \times 0.87,$$

where N is the concentration (μmoles kg^{-1} N) of nitrate (plus nitrite where available) and P is the concentration of soluble reactive phosphate (μmoles kg^{-1} P). The constant (2.90) and multiplier (0.87) were used to force the global mean N^* value to be zero (Gruber and Sarmiento, 1997; Deutsch et al., 2001). The tracer DIN_{xs} is defined as

$$DIN_{xs} = N - 16P.$$

The thermocline distributions of these tracers broadly reflect the global distribution of N_2 fixation and denitrification. Elevated N^* or positive (DIN_{xs}) values indicate a history of net additions of N relative to P, while low values indicate net removal of N due to denitrification.

The global rate of nitrogen fixation has been estimated at $\sim 125 \times 10^{12}$ g N yr^{-1} (Gruber and Sarmiento, 1997) using the tracer N^* (Table 2). A similar rate was determined by Lee et al. (2002), who estimated NCP and N_2 fixation from DIC distributions in nitrate depleted tropical and subtropical waters (N_2 fixation rate is derived by assuming that DIC drawdown in the absence of nitrate is driven by diazotrophy). In the North Atlantic, the rate of nitrogen fixation has been estimated to range from < 1–28×10^{12} g N yr^{-1} (Michaels et al., 1996; Gruber and Sarmiento, 1997; Bates and Hansell, 2004; Hansell et al., 2004). The wide range of values reflects uncertainties with subsurface age models, stoichiometric composition of diazotrophs, the geographic extent of nitrogen fixation, and source water values of preformed excess nitrate of N^*. It is also the case that thermocline geochemical approaches are very different in detail and time scale from calculations based on surface seasonal drawdown of DIC.

Table 2 shows that the geochemical N_2 fixation rate estimates for the North Atlantic vary by more than a factor of 10. Given that the global rate estimate of Gruber and Sarmiento (1997) is derived from their Atlantic basin estimate, we can assume that the uncertainty in their global N_2 fixation rate estimate is at least that large. Similarly, large uncertainties apply to direct N_2 fixation rate estimates, i.e., extrapolations of ship-based in situ N_2 fixation rate measurements to basin and global scales (Capone et al., 1997, 2005). As discussed in Section 2.2, uncertainties of the same magnitude also apply to the denitrification rate estimates (Codispoti et al., 2001).

3.2.4. Summary and implications for functional group modeling

Changes in the chemical properties of the ocean have been used to infer functional group activity. Biogeochemical rates that have been derived from chemical fields include, among other things, net community production, calcification, remineralization and N_2 fixation. These estimates are particularly valuable for large-scale biogeochemical modeling studies because (1) they provide validation data on relatively long temporal and spatial scales that cannot be easily derived using direct rate measurements, and (2) these methods yield rate estimates for specific biogeochemical functions that represent the combined effect of all of the organisms involved. However, the uncertainties in some of these rate estimates are still very large. Although geochemically derived NCP and calcification rate estimates are reasonably well constrained, N_2 fixation rate estimates based upon N^*-type calculations are not. The level of uncertainty in the latter diminishes the usefulness of these rate estimates for validating modeling results at the present time. As with the NCP estimates, the global and regional datasets upon which the N_2 fixation rate estimates are based, are gradually being expanded and improved, which will reduce uncertainties. However, these large error bars also reflect uncertainties in subsurface age models, and assumptions about the geographic extent of nitrogen fixation, the stoichiometry of diazotrophs, and source water values of preformed N^*. Thus, improvements in certainty also need to be made along these other lines.

3.3. The role of functional groups in export

Calcite and silica production are important determinants of export flux because they provide ''ballast''. What do we know about the role of mineral ballast in controlling export variability and how well do our models represent this?

An important goal in many biogeochemical modeling efforts is to model and ultimately predict export flux variability. Organic matter and mineral fluxes that reach the deep ocean are of particular interest because these drive large-scale biogeochemical cycles in the ocean and can result in long-term storage of carbon and other elements. For modeling

Table 2
Global and regional estimates of N_2 fixation rates and denitrification rates in the oceans ($Tg\,N\,year^{-1}$).

Method	Annual NCP $10^{12}\,g\,N\,yr^{-1}$)	Reference
New sources of N to the global ocean (N_2 fixation, atmospheric deposition, river input)	238	Gruber and Sarmiento (2002)
N_2 fixation		
Global		
N/P stoichiometry (N*)	125	Gruber and Sarmiento (1997)
North Atlantic Ocean		
N/P stoichiometry (N*)	28[a]	Gruber and Sarmiento (1997)
N/P stoichiometry (N*)	~14–30	Michaels et al. (1996)
N/P stoichiometry (DIN_{xs})	~4.3	Hansell et al. (2004)
N/P stoichiometry (DIN_{xs})	~0.8–4.7[b]	Bates and Hansell (2004)
Denitrification		
Global		
N/P stoichiometry (N*)	175	Gruber and Sarmiento (1997)
N/P stoichiometry (N*)	240 ± 2.7	Codispoti et al. (2001)

[a]This value includes excess nitrate in the Gulf of Mexico.
[b]This value is limited to the subtropical mode water of the North Atlantic ocean only.

these fluxes, it is perhaps best to take a "bottom-(of the ocean)-up" view: The critical state variables to include in models both at the surface and in intermediate layers are determined by the need to model deep fluxes.

All dynamic biogeochemical models must include a representation of export flux at some level because it is necessary to reproduce the characteristic surface depletion and deep-water enrichment of nutrients that is observed in all stratified ocean regions. Representations of these processes vary from simple parameterizations in which the logarithm of the downward flux of organic matter is a linear function of the logarithm of depth (Betzer et al., 1984b; Martin et al., 1987; Pace et al., 1987), to more mechanistic formulations that involve explicit representation of sinking and remineralization of detritus particles (Hood et al., 2003). It has become common practice in more recent modeling efforts to include two size classes of sinking particles, which allows representation of fast and slowly sinking components of the export flux (Christian et al., 2002a, b; Moore et al., 2002a, b; Wiggert et al., 2004, 2006). All of these methods are simplifications that work (to first order) in that they reproduce the exponential decline in export flux observed in the ocean (Martin et al., 1987).

However, it has long been recognized that mineral material (calcite and silica) play an important role in driving export to the deep ocean (Francois et al., 2002). Recently it has been shown that there is a strong quantitative relationship between organic carbon (POC) flux and the flux of mineral ballast (Armstrong et al., 2002). By fitting a series of models to data from the US JGOFS EqPac study, these authors found that using total mineral material as a predictor of POC flux dramatically increased the predictive power of both exponential and power-law (Martin curve) remineralization profiles. In a related study, Klaas and Archer (2002) collected global data on POC flux and the fluxes of individual mineral ballasts. They fit a simple linear regression equation

$$\mathrm{POC}_{\mathrm{flux}}(z) = a\mathrm{Si}_{\mathrm{flux}}(z) + b\mathrm{CaCO}_{3\,\mathrm{flux}}(z) + c\mathrm{Dust}_{\mathrm{flux}}(z),$$

where $\mathrm{Si}_{\mathrm{flux}}(z)$, $\mathrm{CaCO}_{3\mathrm{flux}}(z)$, and $\mathrm{Dust}_{\mathrm{flux}}(z)$ are the measured fluxes of silica, calcite and dust as a function of depth (z), with dust flux estimated from aluminum or titanium. They found, rather remarkably for biogeochemical studies, that this simple equation (which assumes constant POC:silicate, POC:carbonate, and POC:dust with depth) explained 85–90% of the variance at depths >2000 m, whereas reliance on a single predictor variable (such as silica) explained only 50–60% of the variance. In addition, they found that at these depths, silica transported only 3–4% (by mass) of POC, whereas carbonate and dust transported

5–6%, so that carbonate is clearly a more efficient transporter of POC.

It also has been long established that organisms associated with specific functional groups, like silica-producing diatoms, can have a profound impact on sinking rate through their influence on particle aggregation (Alldredge and Gotschalk, 1989). For example, aggregation and mass sinking after the spring diatom bloom in temperate latitudes is almost certainly driven by a combination of both ballast and aggregation effects. Models that account for the effects of particle aggregation on sinking flux range from sophisticated mechanistic formulations that take into account factors such as particle "stickiness" and collision rate in coagulation processes (e.g., Jackson, 1990, 2001) to simple parameterizations in biogeochemical models that accelerate sinking rate when phytoplankton concentrations are high (e.g., Hood et al., 2003).

It is clear from these examples that incorporating functional diversity also may be essential for modeling export. It is a bit daunting, however, to recognize that the functional diversity needed to achieve these goals may rely as much on representing the functional diversity of zooplankton as that of phytoplankton. More than half of the carbonate flux in deep sediment traps can be due to foraminiferal (zooplankton) tests in the Arabian Sea (W. Prell, personal communication). As we discussed above in Section 2.4, there have been numerous attempts to explicitly include calcification and export associated with coccolithophorid production in biogeochemical models, but few, if any, have attempted to include forams or other higher trophic level calcifiers. This is a direct consequence of (1) the fact that we know so little about the physiology and ecology of higher trophic-level calcifiers, and (2) our inability to directly assess their calcification rates and/or biomass variability.

It is probably fair to say that the modeling community has been focused for too long on euphotic zone productivity and export, and that it has neglected the coupling between export from the euphotic zone and export to depth. The mesopelagic zone (which we define here as the region extending from the base of the euphotic zone to ca. 1000 m in the open ocean) is a critical region for particle transport and remineralization. In this region, particle flux decreases by orders of magnitude due to rapid remineralization of the more labile components of the sinking particles. Yet we know remarkably little about this zone. The depth at which remineralization occurs is a function of both remineralization rate (i.e., lability) and sinking rate. Ballasted or aggregated particles that sink rapidly can escape mesopelagic remineralization and thus provide an important mechanism for transporting organic matter to greater depths.

In addition to the ballasting and aggregation effects discussed here, export is strongly influenced by several other biogeochemical processes, including the production, packaging and sinking rate of fecal pellets, zooplankton vertical migration and excretion, and seasonal mixing of DOM. In most models, most of the export is driven by the former, i.e., detritus produced by zooplankton. There are also two tightly held and somewhat contradictory paradigms in the marine biogeochemical research community that are usually not fully accounted for in the models: (1) that diatoms are associated with export from the euphotic zone and (2) that the majority of export to the deep ocean is associated with calcium carbonate flux (Honjo, 1996; Klaas and Archer, 2002). The co-existence of these contradictory paradigms appears to be a consequence of the fact that marine ecosystem modelers tend to have either a "top-down" or "bottom-up" perspective. Both of these viewpoints are correct at some level, i.e., diatoms can enhance particle sinking rates and drive significant flux events through their influence as ballast and on aggregation, and higher trophic level calcifiers like forams are crucial determinants of deep-ocean calcite and carbon fluxes, because they sink like rocks. Perhaps these views could be reconciled if foraminifera consume sinking diatom aggregates on their way through the mesopelagic! If these kinds of ballasting, aggregation and food web interactions are important determinants of export and sinking rate, then modeling them may be imperative in order to adequately characterize fluxes to the deep sea both now and in the future.

3.4. Higher trophic levels and grazing in functional group modeling

Biogeochemical functional groups in the ocean are composed of a broad suite of organisms that span multiple trophic levels. Moreover, grazing and top-down regulatory interactions almost certainly influence the expression of these functions among all trophic levels. Despite these obvious complexities, the state-of-the-art of marine ecosystem modeling is based on simplistic and primitive representations of

grazing interactions and mortality functions. Do we need to focus more on the role of higher trophic levels and grazing in our models?

The organization of pelagic ecosystem models by functional groups requires a different perspective on grazing processes and trophic interactions than, say, a model structured on the basis of organism size. For one, a sized-based model is more intuitive in terms of predator–prey coupling and can, arguably, be validated or tuned more easily with the kinds of data that are readily collected in routine ocean sampling (e.g., size-fractioned chlorophyll, POC and zooplankton). For another, in plankton functional groups, the chemistry of shells and skeletons is weighted more heavily than basic trophic functionality, like auto- and heterotrophy. Diatoms are grouped with radiolarians (the "silicifiers"), and coccolithophores are mixed with foraminifera and pteropods (the "calcifiers"). Such groupings inherently confound carbon and mineral flows within and out of the euphotic zone, but do they lead to a better understanding of the fate(s) of exported material?

For autotrophs with mineral tests, for example, there is only one source—the euphotic zone. For similarly grouped heterotrophs, on the other hand, there are multiple places throughout the water column where they can intercept and interact with sinking particles and/or synthesize new mineral structures, unencumbered by nutrient limitations (e.g., Si) in overlying surface waters. Unlike carbon-based models, where the composition of sinking organic matter can be modified at depth but must always diminish relative to its source in surface waters, there is no comparable constraint on mineral precipitation. Thus, adequate prediction of silica and carbonate fluxes would seem to require basic knowledge of the ecologies and process rates of relatively exotic heterotrophs—foraminifera, radiolaria and pteropods—that are generally ignored in experimental process studies emphasizing dominant trophic pathways. The vast extent of the skeletal oozes of such organisms in marine sediments also would argue that they be properly considered in models organized by "function" if the primary goal is to model export and deep-ocean fluxes. This argument however, may not hold for modeling water-column chemistry in the present-day ocean because the deep-ocean fluxes of calcium, silica and carbon represent only a small fraction of their global export.

As we touched upon briefly at the end of the previous section, whether other grazers and grazing processes really "matter", in the sense of requiring detailed model parameterization of explicitly defined functional groups of consumers, gets to the crux of differing viewpoints on the relative importance of bottom-up and top-down regulation of marine communities. The former school maintains that the nature of pelagic food webs is largely determined by the phytoplankton response to ocean physics and nutrient inputs, a point of view expressed in the following quote from Cullen et al. (2002): "Copepods and whales do not determine which groups of plants shall flourish: like phytoplankton, they are themselves expressions of the regional physical oceanographic regime". The counter-argument is that the increases or decreases of different phytoplankton taxa in a mixed assemblage do not follow directly from their instantaneous growth rates, but from the much smaller net differences between their growth rates and mortality losses. This suggests that the trajectories of community change cannot be predicted without adequate knowledge of both growth and mortality processes (Verity and Smetacek, 1996; Banse, 2002).

There is reasonable evidence in support of both viewpoints. Diatoms do tend to dominate shallow euphotic zones that are turbulent and nutrient replete (Margalef, 1997), and they are the predictable responders to iron fertilization of HNLC waters (Coale et al., 1996, 2004; Boyd et al., 2000). Coccolithophores and/or other prymnesiophytes typically follow diatoms in seasonal succession when silicate is depleted (Margalef, 1997). Stratified, oligotrophic conditions select for nitrogen fixers. On the other hand, the diatom response to iron fertilization occurs against a backdrop of demonstrable grazer control of other fast-growing but smaller phytoplankton (e.g., Landry et al., 2000). Variations in the abundance of predatory jellyfish (e.g., the moon jelly *Aurelia*) can significantly alter the community composition of both the zooplankton and phytoplankton (Schneider and Behrends, 1998). Salps appear capable of controlling phytoplankton communities and bloom occurrence over significant regions of the Southern Ocean (Dubischar and Bathmann, 1997). In addition, trophic cascades from whales can exert a strong influence on marine algal assemblages, albeit of the benthic kind (Estes et al., 1998). Perhaps even more relevant is the existence of well-documented trophic cascades in some lakes with simple ecosystems

(Carpenter et al., 1985). How do we reconcile such different perspectives in structuring marine ecosystem models?

One key might be to recognize and account for the evolved adaptations of certain phytoplankton to minimize or at least reduce, their vulnerabilities to pelagic consumers (Verity and Smetacek, 1996). The relatively good modeling success that has recently been achieved for *Trichodesmium* (e.g., Hood et al., 2001, 2004; Moore et al., 2002a, b) can serve as an interesting example. By most accounts, *Trichodesmium* is a slow-growing noxious primary producer, unpalatable to all but a few species of relatively rare harpacticoid copepods. Increases and decreases of *Trichodesmium* are thus governed by environmental factors other than grazing, and their blooms and distributions may be more environmentally predictable as a consequence. Chemical grazer deterrants may play similarly important roles in the environmental responsiveness of other bloom-forming species and groups. For example, DMS-producing clones of *E. huxleyi* are virtually ignored as prey by the dinoflagellate *Amphidinium longum* compared to clones that do not produce DMS (Strom et al., 2003). In mixtures of toxic and non-toxic species of morphologically similar dinoflagellates, the copepod *Acartia tonsa* easily discriminates and feeds almost exclusively on the non-toxic form (Teegarden, 1999). Many diatoms produce aldehydes that, when ingested in high concentrations, inhibit the development of copepod eggs (e.g., Miralto et al., 1999), thus slowing their reproductive and numerical response to a developing bloom. These defenses are in addition to the more recognized structural or morphological features (e.g., spines, thick tests, the membranous sacs of *Phaeocystis*) of many bloom-dominating species that discourage grazers. Such adaptations indicate that grazing losses clearly do matter on an evolutionary time scale. However, they also may explain why certain outcomes in community composition or succession seem environmentally pre-determined. For example, grazing deterrence is included as part of Margalef's theory of plankton succession (Margalef, 1978), i.e., resistance to grazing is selected for in the high-nutrient low-turbulence regime (see also Riegman, 1998; Smetacek, 1998). Clearly though, we need to know more about the extent of such predator defenses and the advantages that they confer on functional groups or specific taxa under various environmental circumstances.

Despite the comments above, it is not the general rule that phytoplankton escape grazing; thus, the different sources of mortality still need to be reasonably represented in models to understand mechanisms and relationships. For example, the anti-grazing defenses of *Trichodesmium* may facilitate the ability of modelers to predict its occurrence from a knowledge of growth conditions, but the models may still miss the mark with respect to activity levels of the N_2 fixation "function". As noted previously, organisms of different sizes and vulnerabilities are important contributors to this function, and those particularly in the nanoplankton size range (Zehr et al., 2000) will likely experience strong top-down regulation within the microbial community (e.g., Calbet and Landry, 1999).

Given this mixed bag of interactions, how one might define grazer functional groups in relation to phytoplankton functions is a particularly vexing problem. We are intuitively drawn to distinguishing roles of various macro-consumers such as salps and copepods, which interact with particle fields and contribute to export in qualitatively different ways. However, the details of these relationships are still far from clear. Copepods are a diverse group with feeding characteristics ranging from suspension-feeding to carnivory, and their relative positions in the planktonic food web vary regionally. Regarding salps, it is not known, for instance, whether they can control or are generally controlled by the occurrence of phytoplankton blooms, or whether their greater efficiency in turning ingestion to export under low food conditions leads to a greatly different net export from surface waters compared to that driven by the lower efficiency of copepods under their typical higher food conditions.

While these points are certainly worthy of further exploration, we should not lose sight of major disconnects between grazing reality and parameterizations in current models of marine plankton. Zooplankton are the highest trophic level represented in most marine biogeochemical models, with grazing typically specified using classical functional forms, i.e., Holling's type I–III functions or power curves. One (or some combination) of these functions is also usually used to specify the zooplankton mortality, or "closure" in the model. Suffice it to say that these standard approaches for specifying the top down control in biogeochemical models are extremely crude compared to the foregoing discussion. Moreover, it is well known that these different

grazing formulations have a profound impact on model equilibrium solutions, stability and trophic transfer (Steele and Henderson, 1992; Kemp et al., 2001; Gentleman et al., 2003).

It is also common, for example, to distinguish the fates of diatoms from "other" phytoplankton in models as if they were all of such a size or morphology to be only vulnerable to larger metazoan consumers. The reality is that much, if not most, of diatom production in the open ocean may be consumed by large protists (dinoflagellates and ciliates). Such consumers, not metazoans, rapidly responded to the diatom-dominated bloom in IronEx II, matching high diatom growth rates with high grazing mortality after only a few days, and maintaining an efficient recycling system (Landry et al., 2000). In AESOPS and SOFeX, protist grazers, not metazoans, accounted for the majority of grazing impact, taking 50–90% of phytoplankton production, even when these Southern Ocean waters were strongly dominated by large diatoms (Landry et al., 2002; Landry, unpublished). Because protistan consumers handle diatoms as individual cells and produce individual empty frustrules, the implications of their grazing activity for Si and organic recycling and C:Si export ratios are quite different from organisms that repackage concentrated egesta into large fecal pellets.

The simple fact is that ecosystem models are notoriously sensitive to grazing parameterizations. Even if the modeling community is able to come up with good models of the growth dynamics of different phytoplankton functional groups, there is a question of whether the resulting ecosystem models will perform well because of sensitivity to the loss terms, which are often poorly understood. One of the great challenges in functionally organized models will be determinng how to represent the interactions of multiple dominant trophic pathways with each of the defined functional groups, without resorting to an overly complex superstructure based on size or some other predator–prey defining relationship.

3.5. Do we need to represent DOM and heterotrophic bacteria explicitly in our models?

Bacteria are responsible for a large fraction of the respiration and recycling in the ocean, as well as providing a potentially important "link" for cycling DOM and detritus to higher trophic levels. How important is the role of DOM in marine biogeochemical cycles? Do we need to include explicit representations of DOM and bacteria in our models?

Several extensive reviews of phylogeny and ecological function of specific prokaryotic groups (Gray and Head, 2001; Kirchman, 2002, 2004; Rappé and Giovannoni, 2003) and DOM characterization and bioreactivity (Benner, 2002; Carlson, 2002) exist in the literature. We will begin with a general discussion of the topic of heterotrophic prokaryotes and DOM remineralization and then address the specific (and somewhat contentious) question of whether or not bacteria and DOM cycling need to be explicitly represented in biogeochemical models.

3.5.1. Heterotrophic prokaryotes and DOM remineralization

Biological reactivity of DOM encompasses a broad continuum, from refractory material that turns over on time scales of centuries to millennia (Williams and Druffel, 1987; Bauer et al., 1992) to very labile material that turns over on time scales of minutes to days (Fuhrman and Ferguson, 1986; Keil and Kirchman, 1991; Cherrier et al., 1996; Rich et al., 1997). A third pool of bioavailable DOC, which was first identified by Ogura (1972), is available to heterotrophic prokaryotes, but with turnover time scales of months to years. More recent field studies have shown that a portion of this "semi-labile" DOC pool, which accumulates seasonally in surface subtropical waters, can provide a significant pathway for export if it escapes heterotrophic remineralization long enough to be removed horizontally or vertically by physical processes (Kirchman et al., 1993; Carlson and Ducklow, 1995; Cherrier et al., 1996).

DOM transformations between refractory, semilabile and labile forms are driven by both biotic and abiotic factors. Free-living heterotrophic bacteria are recognized as the dominant processors and consumers of DOM in the ocean (Azam and Hodson, 1977). The traditional view of their ecological role within the microbial loop is to facilitate transformations of DOM to POM or to remineralize DOM back to inorganic constituents (Ducklow et al., 1986; Goldman and Dennett, 2000). However, through the action of their extracellular hydrolytic enzymes bacteria mediate the transformation of DOM from high-molecular-weight to low-molecular-weight compounds (Hoppe, 1991; Smith et al., 1992; Christian and Karl, 1995), which can then be transported through

their cell membranes. In addition, UV excitation from sunlight plays an important role in mediating DOM transformations in surface marine waters. In particular, several studies have demonstrated that photochemical degradation of refractory DOM can lead to formation of biologically available low-molecular-weight compounds (Kieber et al., 1989; Mopper et al., 1991; Moran and Zepp, 1997). Photochemical processes also can release labile N and P compounds such as ammonium, amino acids and phosphate (Moran and Zepp, 2000).

The percentage of net community production that is partitioned as DOM appears to vary in space and time from 10% to 70% (Hansell and Carlson, 1998). The variability of DOM production may be related to nutrient regime, community structure and physiological state of the planktonic community. In addition, the quality of annually produced semi-labile DOC represents a broad continuum of lability that does not appear to be turned over at uniform rates. For example, in the Sargasso Sea a significant fraction of the semi-labile pool persists on time scales of greater than a year, while the entire semi-labile pool in the Ross Sea turns over on a time scale of <1 year (Carlson et al., 2000). A portion of this variability corresponds to the composition of the semi-labile DOM pool. The majority of the DOM pool remains uncharacterized; however, significant advances have been made in assessing the bioreactivity of DOM in oceanic systems (see reviews by Skoog and Benner, 1997; Biersmith and Benner, 1998; Benner, 2002).

The partitioning of bulk DOM into various pools of bioavailability was designed to help provide a conceptual framework for which DOM turnover could be modeled. Use of the semi-labile DOM pool in recent models has helped improve the predicted distributions of $\delta^{14}C$ values and nutrient fields in GCMs (Yamanaka and Tajika, 1997), and DOC and DON dynamics of some one-dimensional models, e.g., Anderson and Williams (1999). However, while model formulations and predictions have improved, the formulation of DOM production and cycling in most models is still vastly oversimplified compared to reality (Christian and Anderson, 2002). For example, DOM production is often assumed to be a constant fraction of primary production or of particulate organic matter (POM) stocks. Further, DOM consumption is often assumed to be a constant fraction of bacterial biomass (BB) or bacterial production (BP) rates and usually only labile or semi-labile forms of DOM are represented. In calculating the turnover of the semi-labile DOM pool it also is often assumed that all prokaryotes are capable of remineralizing all DOM components equally. (See Christian and Anderson (2002) for a recent review of the state of the art in modeling DOM biogeochemistry.)

3.5.2. All heterotrophic microbes do not utilize all DOM components similarly

Significant diversity of prokaryotic communities exists in oceanic systems (Rappé and Giovannoni, 2003; Venter et al., 2004). Vertical stratification of major prokaryotic groups between the oceanic euphotic and aphotic zone has been observed (Giovannoni et al., 1996; Karner et al., 2001; Morris et al., 2002). The mechanisms responsible for spatial variability of prokaryotic domains or subdivisions over depth are not well understood. However, recent experiments (e.g., Carlson et al., 2002) and conceptual models provide compelling reasons to believe that the growth rates of specific heterotrophic microbial populations in planktonic ecosystems are linked to the composition and amount of DOM, as well as to the availability of inorganic nutrients. Thus, detailed modeling of DOM cycling and composition may be a prerequisite for simulating the spatial variability of different prokaryotic groups. As discussed below, current models typically represent prokaryotes as a single, homogeneous "bacteria" group.

Organisms in the bacterial and archaeal domains represent a vast range of metabolic strategies. In some cases there are clear linkages between genetic identity and function (Gray and Head, 2001), e.g., sulfur reducers, ammonia-oxidizing bacteria and photoautotrophic bacteria. However, linking diversity of prokaryotes to subtle differences in function is more problematic among the broad group of prokaryotic heterotrophs, especially because the vast majority have not been cultured. At this point, all we can say is that a diverse assemblage of prokaryotes is essential for the complete degradation of DOM (Cottrell and Kirchman, 2000).

The recent discovery of significant contributions to the carbon cycle of aerobic anoxygenic photosynthetic bacteria (e.g., Kolber et al., 2001) and bacteria that contain proteorhodopsin (Bejá et al., 2000) in the euphotic zone of the ocean indicates that photoheterotrophic processes may be more significant than once thought. Photoheterotrophy is a metabolic process by which prokaryotes utilize light as an energy source and organic matter to meet

all or part of their C requirement. Archaea also comprise a significant portion of prokaryotic biomass in the mesopelagic and deep ocean (Karner et al., 2001), yet little is known about how these prokaryotes interact with DOM. The presence of photoheterotrophs and Archaea as well as various subdivisions of heterotrophic bacterioplankton implies that our conceptual models of heterotrophy and DOM remineralization in the ocean may change (Kirchman, 2004). It is clear that much work is needed to better characterize the interactions of various heterotrophic prokaryotic groups with DOM in order to determine the appropriate phylogenetic level to include in models.

3.5.3. Do we need to represent heterotrophic bacteria and DOM explicitly in our models?

Heterotrophic bacteria certainly play a central role in driving marine biogeochemical cycles. They are responsible for a large fraction of the respiration and recycling in the ocean (Rivkin and Legendre, 2001), they provide an important link for cycling DOM to higher trophic levels (Ducklow et al., 2001), and they can compete with phytoplankton for both organic and inorganic nutrients (Kirchman, 2000). Moreover, specific groups of bacteria are directly responsible for mediating two key N-cycle functional groups: nitrification and denitrification (Codispoti et al., 2001). The microbial foodweb also has gained increasing attention in the various roles it plays in controlling export of biogenic carbon from the surface oceans and vice versa (Michaels and Silver, 1988; Legendre and LeFevre, 1995; Legendre and Rassoulzadegan, 1996; Rivkin and Legendre, 2001). Based upon these considerations, it has been argued that bacteria must be represented explicitly in biogeochemical models (Ducklow, 1994; Kirchman, 2004; Pomeroy, 2004). Yet most large-scale biogeochemical models do not explicitly represent bacteria (e.g., Oschlies and Garç on, 1999; Christian et al., 2002a, b; Moore et al., 2002a, b, 2004; Gregg et al., 2003; Hood et al., 2003). Rather, these models have simple parameterizations of the net effects of bacteria on the C, N and P cycles, where dissolved and particulate organic matter are remineralized directly to inorganic nutrient pools.

But how can we model the cycles of the various elements in the ocean without explicitly including one of the primary agents that remineralize them? The practice has its origins in the history of open-ocean biogeochemical model development, which began in the late 1960s and early 70 s (Hood and Christian, 2006). Early biogeochemical model structures were developed before the role of bacteria and the microbial loop in biogeochemical cycles were fully appreciated (Pomeroy, 1974; Williams, 1981; Azam et al., 1983). These models considered the pelagic food web to be dominated by large phytoplankton and mesozooplankton, which could be represented by simple NPZ and NPZD (nitrogen, phytoplankton, zooplankton and detritus) model formulations. The use of these simple, models has persisted to this day (e.g., Steele, 1998; Oschlies and Garçon, 1999; Denman and Pena, 2002; Denman, 2003; Hood et al., 2003) for four reasons: (1) they are simple and relatively easy to diagnose; (2) they are computationally efficient and so can be applied in large-scale GCMs; and (3) they *do* represent the fundamental components of marine food webs that drive export variability, i.e., large phytoplankton and mesozooplankton that produce large organic particles that sink; and (4) they seem to work.

The explicit representation of bacteria in these models is typically dismissed on the grounds that bacteria are ubiquitous (i.e., on the order of 10^5–10^7 per ml), and their biomass and activity tends to co-vary with primary production and organic-matter concentrations. Hence they can be parameterized as a component of the detritus pool. However, these assumptions are gross oversimplifications. While BB and BP are positively correlated at large scales to PB and PP, respectively, there is significant variability in the ratios of these parameters among various ocean systems. Although it is often assumed that BP represent 30% of local PP, Cole et al. (1988) and Ducklow (1999) summarized bacterioplankton and phytoplankton properties from seven oceanic sites and observed BP:PP ratios ranging from 0.04 in the Ross Sea to 0.26 in the Equatorial Pacific. Ducklow (1999) also reported that BB:PB ranged from 0.02 in the Ross Sea to 1.2 in the Arabian Sea. Thus, assuming a constant relationship between bacterioplankton and phytoplankton and detritus properties in models is not appropriate for all oceanic regimes and may be a poor assumption for global applications.

Based on these considerations, many marine microbiologists have argued persuasively that explicit representation of bacteria must be included in biogeochemical models (Ducklow, 1994; Kirchman, 2004; Pomeroy, 2004). In practice, the level of phylogenetic resolution to be included will ultimately depend on the question asked. In the context

of this paper, the questions revolve around predicting how marine biogeochemical cycles may change in response to global warming. Most marine ecosystem models that include bacteria contain only a single compartment to represent heterotrophic prokaryotes, both bacteria and archaea. The food web model of Laws et al. (2000), for example, explicitly includes one heterotrophic bacteria state variable. The model does an excellent job of reproducing field observations of export ratios in the open ocean and at the same time explains the variability in phytoplankton/heterotrophic BB across a wide spectrum of both marine and freshwater pelagic communities (Laws, 2003). Cottrell and Kirchman (2000) suggested that more realistic marine models might include three broad bacterial groups (α and γ proteobacteria and *Cytophaga-Flavobacter*). Unfortunately, few quantitative data exist regarding the distribution patterns or metabolic variability of these groups in the ocean.

Many of these arguments (both the pros and the cons) apply to DOM as well. A great deal of modeling work has been undertaken with models that include DOM. Yet, as we touched on above, there are many uncertainties in the parameterization of DOM in models, such as the characterization of different fractions, the relative roles of phytoplankton and zooplankton in producing DOM (as well as other sources), and the allocation of production between pools of different lability (Christian and Anderson, 2002). But do we really need to explicitly include DOM in models? As is the case with bacteria, most large-scale biogeochemical models do not include DOM, though some do (e.g., Six and Maier-Reimer, 1996). Popova and Anderson (2002) made a comparison in a global box model of ecosystem models that either did or did not include DOM, but were otherwise alike. Predicted distributions of NO_3 and DIC were similar between the two runs, as was export flux. So one could argue that DOM is not needed in large-scale models. However, there were significant differences in primary production and f-ratio, which could be important when undertaking climate change scenario runs. Along these lines, the model of Pahlow and Vézina (2003) implies that there is a negative relationship between DOM accumulation and temperature that could lead to a strong positive feedback between temperature and CO_2 release from the DOM pool that may help explain the large variations in atmospheric CO_2 between glacial and interglacial periods. Moreover, quite a few regional models have included DOM (and bacteria), and have in some instances indicated that this inclusion is important in biogeochemical cycling in those areas (e.g., Anderson and Williams, 1998; Levy et al., 1998; Bissett et al., 1999a, b; Walsh et al., 1999; Anderson and Pondaven, 2003).

Nonetheless, the fact remains that there is no clear consensus in the modeling community that explicit representation of bacteria and DOM is necessary to model bulk biogeochemical cycling or ocean biogeochemical response to global warming. Current simple model formulations that do not include these components appear to be capable of reproducing first-order biogeochemical variability in the present-day ocean (e.g., Oschlies and Garçon, 1999; Christian et al., 2002a, b; Moore et al., 2002a, b, 2004; Gregg et al., 2003; Hood et al., 2003). The success of these large-scale model applications may be related to the spatial and temporal scales under consideration, i.e., the temporal forcing is usually on the order of days to months, and the spatial resolution in most of these models is 50 km or more. Perhaps it is not necessary to explicitly resolve bacteria, which vary on time scales of hours and space scales of micrometers. A similar argument might be made for labile DOM.

However, these scaling arguments do not address the fact that there is vertical and inter-basin variability in bacteria and DOM composition, abundance and production, which suggests that bacterial and DOM production and loss processes are not simply manifested at the microscale (Ducklow, 2003). Moreover, this scaling argument could equally well be applied to most phytoplankton. Perhaps the honest answer is that we know (or think we know) a lot about phytoplankton based on decades of microscope work, pigment profiles, production rate measurements, physiological studies and large-scale synoptic satellite measurements. By comparison we know relatively little about bacteria. We have more confidence in our models if they reproduce observations, and we have a large database of phytoplankton observations. This has provided the motivation to explicitly model different functional groups of phytoplankton, where most of the progress has been made. We have no analogous suite of observations for bacteria or DOM. Taking this line of reasoning a step further, we can return to the question of why we do not include higher trophic level functional groups, like foraminifera and pteropods, in our models. Perhaps the answer is that, like bacteria and DOM, we have

very few field data to compare with, so we tend to ignore them.

3.6. Data assimilation and functional group modeling

Data assimilation and inverse methods provide powerful new tools to help us construct, compare and improve biogeochemical models. How much will these methods help us achieve our modeling goals and what are the major constraints?

Obviously, there are still many significant gaps in our knowledge and our models of marine biogeochemical cycles, and major challenges remain in terms of developing, parameterizing and validating complex multi-element and multi-trophic-level ecosystem models. Over the last decade, data assimilation techniques have been increasingly applied to help solve some of these problems.

Data assimilation can be used to optimally combine models with available data in order to estimate parameter values and fluxes that are difficult or impossible to quantify directly. (See Hofmann and Friedrichs, 2001, for a review of data assimilation techniques as applied to biogeochemical models.) Data assimilation has become especially useful in recent years in the wake of large-scale studies such as JGOFS and GLOBEC that have provided a wealth of data on a wide range of ecosystem processes.

Two very different data assimilation methods that have recently been applied to ecosystem models of varying complexity are the variational adjoint method (Lawson et al., 1995; Friedrichs, 2002) and the inverse analysis approach of Vézina and Platt (1988) (e.g., Richardson et al., 2004,2006). The variational adjoint method can be used essentially as a non-linear least-squares optimization technique to estimate the best fit of a set of parameters for a given model and dataset. This approach minimizes model/data misfits by adjusting model parameters governing processes such as growth, grazing, remineralization and mortality. Similarly, the Vézina and Platt approach is a least squares optimization technique that provides a description of all fluxes in a food web by using ancillary information to constrain the estimation of unknown flows. The approach includes the use of assimilation and production efficiencies of different groups of organisms together with a description of the flows in the food web (i.e., all possible trophic interactions) and results of field measurements of rate processes (“known” flows). The underlying tenet of the approach as applied to food web modeling is that simple mass balance equations and known biological relationships constrain possible flows when some data on food web structure and flows are known (Vézina and Pahlow, 2003).

Work published to date that has used these approaches has defined “functional” groups in terms of size. The phytoplankton, for example, are often split into size classes such as picoplankton, nanophytoplankton and microphytoplankton. Zooplankton are also frequently compartmentalized into two or more different size classes. Size has been used as the criterion for compartmentalization primarily because data are often available to make the distinctions, and, as we discussed in Section 3.4, the size of the producers and consumers is often a major determinant of the trophic dynamics in marine food webs. The division of model compartments into functional groups (e.g., nitrogen fixers and calcifiers) is currently limited by the availability of data on the abundance and, more importantly, the activity (e.g., rates of nitrogen fixation and calcification) of these functional groups. Some of the functionality is retained when split by size (e.g., autotrophic primary producers in many oligotrophic systems are dominated by the smallest size class, and diatoms are most often included in the microphytoplankton), but, as we discussed in Section 3.4, this compartmentalization based on size would blur distinctions between functional groups if all representatives were contained within the same size class.

If functional group-specific biomass and rate data are available, there is no a priori reason why these data assimilation approaches could not be used with functional groups; however, the lack of rate information even for size-discriminated groups is a common problem. Biomass data are more commonly available (based on phytoplankton pigments or microscopy), and sometimes data are available on size-fractionated primary production or zooplankton grazing. Most often, however, we are forced to apportion bulk estimates into varying size classes based on the contribution of that size class to total biomass (usually measured as total carbon or total chlorophyll *a*). This may not be troublesome in a region like the equatorial Pacific, where the most abundant group of autotrophs, the picoplankton, is also responsible for the majority of the primary production (see Richardson et al., 2004). However, this assumption may not hold in other oceanic regions. In the subtropical and tropical North

Atlantic, for example, measurements of size-fractionated chlorophyll *a* and primary production showed that the relative contribution of the large (>2 μm) phytoplankton to total chlorophyll *a* biomass was smaller than their contribution to total primary production (Fernandez et al., 2003).

The inclusion of functional groups in the Vézina and Platt assimilation approach will require rate measurements for all functions being modeled. Rates of new production, primary production and zooplankton grazing are (relatively) straightforward to measure, which is likely the reason why the currency of many food web and ecosystem models is carbon or nitrogen. Determination of rates and processes pertinent to functional groups like the silicifiers or the calcifiers, including their stoichiometric relationships to carbon, is a more difficult task (Ragueneau et al., 2000; Barker et al., 2003). In contrast, with the variational adjoint assimilation approach rate measurements are not needed for all the functions. Rather, one can assimilate the available data, and attempt to estimate the rate measurements that have not been measured. It is perhaps not surprising that some of the more well-developed ecosystem models that incorporate functional groups focus on the relationship between nitrogen fixers and carbon cycling, as N_2 fixation is a process that can be measured with relative ease in the field (Hood et al., 2001; Fennel et al., 2002). Moore et al. (2002a, b, 2004) and Gregg et al. (2003) have, for example, extended this approach to include other functional groups, e.g., silicifiers (diatoms), nitrogen fixers (diazotrophs) and calcifiers (coccolithophores). However, to our knowledge, there have been no attempts to formally assimilate the available rate and/or biomass data for these functional groups.

3.7. Will increasingly complex models lead to more predictive skill?

Most biogeochemical modeling efforts are based on classic ecosystem modeling approaches. These models are becoming increasingly complex. Will we ever have enough data to constrain and validate these models? Will they ultimately lead to more predictive skill?

Efforts to incorporate organisms into biogeochemical models that fix nitrogen, denitrify, calcify and silicify require additional parameterizations and/or state variables (e.g., Moore et al., 2002a, b, 2004; Gregg et al., 2003). Moreover, we have argued that explicit inclusion of heterotrophic bacteria and more sophisticated representations of grazers also may be necessary. These arguments are clearly pointing us in the direction of developing increasingly complicated ecological models. Now we step back and ask the question: What are the ramifications of increasing the complexity of biogeochemical models? Is it really feasible to include all these functional groups and processes in our models, and will doing so ultimately improve our predictive skill?

Objectively assessing the performance of models containing varying levels of complexity is not a straightforward task. Because model performance is largely a function of time spent tuning unconstrained parameters, it is often unclear whether a given model reproduces a given dataset because of the specific structural characteristics of the model or because more time has been spent tuning the model. Furthermore, models including additional functional groups inherently have more unconstrained parameters. With a larger number of degrees of freedom, a more complex model can often be tuned to reproduce a given dataset as well or better than a more constrained, simpler model. The problem with such parameter tuning is that the complex model may begin to fit noise in the observational data rather than the underlying functional relationships. Another problem with complex models is transfer of variance, whereby functions that have similar effects on the observables are given co-varying weights based on subtle differences in formulation, sometimes giving the right answer for the wrong reasons. When this happens, the predictive ability of the complex model will be lower than that of a simpler model, because only the underlying functional relationship will be common to the original dataset and a second dataset used to test predictive power. The noise in the two datasets will be independent and random, and a function that gives a good fit to one set of random numbers can hardly be expected to have any predictive ability with respect to an independent set of random numbers. The solution to this conundrum is to carry out appropriate statistical tests to determine whether the improvement in goodness of fit obtained with a more complex model is significant compared to the level of noise in the data.

One method of comparing the performance of models of varying complexity is to invoke the formal data assimilation and parameter optimization techniques that we discussed in the previous section. For example, Friedrichs et al. (2006) have used the variational adjoint method of data

assimilation to objectively compare how well three one-dimensional ecosystem models reproduce 1 year of data (chlorophyll, zooplankton biomass, nitrate, export flux and production) from the US JGOFS Arabian Sea Process Study. The three models represent (1) a four-component classic diatom–mesozooplankton ecosystem (McCreary et al., 1996, 2001; Hood et al., 2003), (2) a five-component microbial food web model dominated by small autotrophs and heterotrophic processes (Hood et al., 2001, 2004; Coles et al., 2004) and (3) an eight-component model containing two size classes of phytoplankton, zooplankton and detritus as well as ammonium, essentially representing a combination of Model 1 and Model 2 (Christian et al., 2002a, b).

By means of the variational adjoint method, the model-data misfit, also called the cost function (J) is minimized by systematically adjusting the values of the (10, 16 and 19, respectively) tunable parameters for each model. Friedrichs et al. (2006) also introduce the concept of a predictive cost function (J_p), which is estimated by means of a series of cross-validation experiments. In this case, they sequentially assimilate three of the four seasons of data and use the resulting parameter estimates to determine the model-data misfit for the remaining season. Thus whereas J represents how well a model reproduces an assimilated dataset, J_p represents how well a model reproduces unassimilated data and is thus a better measure of the predictive ability of a model.

Friedrichs et al. (2006) find that prior to assimilation, the three models behave very differently (Table 3), with the model-data misfit for the most complex (Model 3) being much less than that of the simplest (Model 1). After identical data are assimilated into each of the models and all unconstrained parameters objectively optimized (10, 16 and 19 parameters for Model 1, 2 and 3, respectively), the difference between the cost function for the simplest and the most complex models is not significant; both models reproduce the data equally well (see also Matear, 1995 who, using different data assimilation methods and observations from the North Pacific, came to similar conclusions regarding the performance of models with different levels of complexity). However, the predictive cost function for the simplest model is nearly 40% lower (better) than that of the most complex model. The implication is that the most complex model is describing noise in the original dataset, and the price associated with fitting noise is a loss of predictive ability. Stochastic phenomena cannot be predicted with deterministic models.

In a second experiment, Friedrichs et al. (2006) compute J and J_p by optimizing only a subset of the total number of unconstrained parameters for each of the three models. These parameter subsets are carefully chosen to include only uncorrelated parameters to which the cost function is most sensitive. In this case the cost functions are higher than they are when all unconstrained parameters are optimized (Table 3); however, the predictive cost functions (J_p) are lower, suggesting an increase in predictive ability of the models. In particular, the value of J_p for the more complex model has decreased by more than 40%. In addition, there is now no significant difference between the performance of the simplest and most complex models. The implication is that by choosing uncorrelated parameters to which the cost function is most sensitive, tuning models to describe noise can be avoided or at least minimized.

These studies illustrate important results that are pertinent to our discussion of functional groups. Firstly, the performance of a given model depends more strongly on the degree to which the model is tuned than on the degree of complexity or the number of functional groups included. In order to

Table 3
Model data misfit with no assimilation (J_0), cost function (J) and predictive cost function (J_p), for three models of varying complexity

Model	# State variables	J_0	Experiment #1			Experiment #2		
			# Control variables	J	J_P	# Control variables	J	J_P
1	4	20.8	10	6.7	10.9	3	8.9	9.8
2	5	15.2	16	5.1	12.4	4	9.8	12.4
3	8	11.4	19	7.2	18.5	4	8.7	10.2

For Experiment 1, all unconstrained parameters within each model are estimated via the variational adjoint method. For Experiment 2, an optimal subset of model parameters is estimated. Uncertainties are ± 0.5. Adapted from Friedrichs et al. (2006).

objectively and optimally tune a model, data assimilation and parameter optimization techniques are essential; however, when employing such techniques with complex multi-functional group models, care must be taken to avoid fitting noise by estimating too many unconstrained parameters. Doing so may improve model-data fit for a given dataset, but can significantly degrade predictive ability. Just as the performance of the models assessed by Friedrichs et al. (2006) decreased/declined as the number of unconstrained parameters increased, continuing to add complexity and functional groups to an ecosystem model and increasing the number of parameters that cannot be constrained with available data may lead to a decrease in predictive ability.

4. Summary and conclusions

In this paper, we have attempted to review the state of the art and major challenges in current efforts to incorporate specific biogeochemical functional groups into biogeochemical models. This discussion has been focused on models that can be applied on basin-wide and global scales in coupled, three-dimensional applications, with an emphasis on prediction, i.e., developing models that might ultimately be used to predict how biogeochemical cycles in the ocean will be altered by climate change and global warming.

We have defined the term "biogeochemical functional group" following Totterdell et al. (1993) and Falkowski et al. (2003) to refer to "biogeochemical guilds", i.e., groups of organisms that mediate a suite of *specific* chemical reactions that drive biogeochemical cycles in the ocean (though we deviate from this definition in considering bacteria and grazing effects). It is important to emphasize that according to this definition "functional groups" have no phylogenetic meaning—these are composed of many different species with common biogeochemical and/or ecological functions. Although this is a useful definition for thinking about how different biogeochemical reactions can be mediated by a large suite of organisms, it poses a major challenge for the biogeochemical modeling community because it underscores the fact that we may need to dynamically represent multiple species and multiple trophic levels in order to fully capture a particular process, like calcification, in models.

Based on our review of the state-of-the-art, we conclude that substantial progress has been made in the last decade toward quantifying the rates of these various functions and understanding the factors that control them. And for some of these groups fairly sophisticated models have been developed that incorporate this understanding. In particular, the understanding of the factors that control diazotrophs (i.e., *Trichodesmium*), silica producers (diatoms) and calcifiers (e.g., coccolithophorids and specifically *E. huxleyi*) is fairly well advanced. This understanding has fueled considerable progress in the development of models that represent these functions. In contrast, modeling of contemporary DMS biogeochemical cycling and the organisms involved (e.g., dinoflagellates and prymnesiophytes) is still in its infancy, and many significant problems remain. Future endeavors to improve estimates of DMS flux based on traditional observational approaches should focus on deriving more accurate estimates of DMS rate processes and their functional dependencies. More estimates of the air–sea flux are also needed to help constrain model results.

We also point out that representations of nitrogen fixation and calcification in current models are incomplete, i.e., based primarily upon models of *Trichodesmium* and *E. huxleyi,* respectively. In fact, many other organisms in the ocean contribute significantly to these functions, but we lack the information required to incorporate them into models and validate the fluxes they drive. Moreover, although nitrogen fixation, calcification, silicification and DMS production are important biogeochemical processes in the ocean, they represent only a small subset of the total, which also include denitrifiers, nitrifiers, anammox, methane produces, methane oxidizers, sulfide oxidizers, sulfate reducers and many others. In particular, there has been surprisingly little attention paid to denitrification in open-ocean biogeochemical modeling efforts even though this reaction mediates the transfer of nitrogen from the ocean to the atmosphere, i.e., it is a crucial term in the oceanic N budget. It is probably also fair to say that, in spite of the fact that we have learned a tremendous amount about the distributions and biogeochemical impact of bacteria in the ocean in recent years, this improved understanding has not yet been incorporated into models. Whether or not we need to incorporate bacteria and other functional groups in models ultimately will be guided by the questions. For the purposes of this paper, these questions revolve

around using biogeochemical models to predict how the ocean will respond to global warming. For example, if the questions involve determining how the global N inventory might change in the future, then obviously it will be crucial to include dynamic functional groups for nitrogen fixation and denitrification.

Another obvious gap is that virtually all functional group modeling efforts have focused on autotrophic microbes, while higher trophic levels have been completely ignored. For example, most dynamic models of calcification have focused on *E. huxleyi* because it can be detected in satellites, even though we know that foraminifera can contribute more than 50% of the deep-ocean calcite flux. Thus, it appears that in some cases incorporating higher trophic levels may be essential not only for representing a particular reaction, but also for modeling export. Moreover, proper represention of grazing mortality may be important for predicting trajectories of community change. Clearly, one of the great challenges remaining in functional group modeling is representing the various impacts of higher trophic levels. This example also highlights another serious problem: we tend to model the organisms for which we have the most validation data (e.g., diatoms, coccolithophorids, *Trichodesmium*) even when they represent only a fraction of the processes we are trying to represent. Bacteria are, perhaps, the most glaring example of this tendency, i.e., they are not explicitly represented in most large-scale biogeochemical models even though they are major drivers of biogeochemical cycling in the ocean because we generally lack global data on their biomass, composition and rate variability.

When we step back and look at the paleoceanographic record, it suggests that oxygen concentrations have played a central role in the evolution and emergence of many of the key functional groups that influence biogeochemical cycles in the present-day ocean, both directly and also indirectly by influencing the availability of trace metals, particularly iron. However, it is not likely that climate change over the next century will significantly alter oxygen concentrations and the redox potential of the oceans. Rather, it is likely that more subtle effects will be important, such as changes in silicate supply or turbulence that can influence the relative success of diatoms versus dinoflagellates, coccolithophorids and diazotrophs. In general, inferences drawn from the paleoceanographic record suggest that global warming will tend to favor the latter because it will give rise to increased stratification. However, other factors, such as potential decreases in oceanic pH and reductions in Fe deposition in the future might reduce the success of coccolithophorids and diazotrophs.

This paper has emphasized that there are still many gaps in our knowledge about the structure of marine ecosystems and that major challenges remain in terms of developing, parameterizing and validating complex biogeochemical/pelagic ecosystem models. Over the last decade, data assimilation techniques have been used increasingly to help solve some of these problems. Two very different methods that have recently been applied to ecosystem models of varying complexity are the variational adjoint method for specifying model parameters and the inverse analysis approach for inferring the relative importance of various trophic pathways. To our knowledge, there have been no attempts to assimilate formally the available rate and/or biomass data for the major functional groups like nitrogen fixers, calcifiers and silicifiers. However, the variational adjoint method has been recently applied in quantitative model intercomparison studies in an effort to assess the costs and benefits of increasing model complexity. Although this review has implicitly suggested that there is a need to include more details and functional groups in models, these intercomparison studies show that adding complexity and functional groups to ecosystem models and increasing the number of parameters that cannot be constrained with the available data can lead to a decrease in predictive ability (see also Denman, 2003; Anderson and Totterdell, 2004).

It is important to remember that capturing the present-day variability tells us little about how well a particular model can predict the future. Very few biochemical modeling studies have carried out rigorous assessments of predictive skill, instead gauging success based upon the goodness of the fit to the available data after tuning to those very same data. If the goal is to develop models that can be used to predict how the oceans will respond to global warming, then we must make quantitative assessments of predictive skill, i.e., by using different datasets for model tuning versus skill assessment. Although we have cautioned that more complex models with more unconstrained parameters may have less predictive ability, we can take some comfort in the notion that this is of little

consequence if we know how well our models predict observations that have not been used for tuning and are satisfied with the results. We also suggest that we may be able to get by with *relatively* simple ecosystem models if the goal is to predict long-term global responses. This is in contrast to, for example, a model that is intended to simulate seasonal and interannual variability at a particular location in a specific ocean basin, i.e., we should be able to predict the future without reproducing all the minute details of the biogeochemical variability along the way.

Acknowledgments

This synthesis paper emerged from a series of principal investigator meetings sponsored by the US JGOFS Synthesis and Modeling Project. Financial support for these meetings was provided by the NSF through the US JGOFS Project Office at Woods Hole. Most of the contributing authors benefited from this support and/or direct NSF SMP funding.

We thank John Cullen, Tom Anderson and Mick Follows for providing thoughtful and in-depth reviews of this paper. The lead author specifically acknowledges NSF Grant nos. OCE-9818708 and OCE-9981218. This paper represents UMCES contribution no. 3908.

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