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REVIEW

Phytoplankton in a changing world: cell size and elemental stoichiometry

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Global increases in atmospheric CO_2 and temperature are associated with changes in ocean chemistry and circulation, altering light and nutrient regimes. Resulting changes in phytoplankton community structure are expected to have a cascading effect on primary and export production, food web dynamics and the structure of the marine food web as well the biogeochemical cycling of carbon and bio-limiting elements in the sea. A review of current literature indicates cell size and elemental stoichiometry often respond predictably to abiotic conditions and follow biophysical rules that link environmental conditions to growth rates, and growth rates to food web interactions, and consequently to the biogeochemical cycling of elements. This suggests that cell size and elemental stoichiometry are promising ecophysiological traits for modelling and tracking changes in phytoplankton community structure in response to climate change. In turn, these changes are expected to have further impacts on phytoplankton community structure through as yet poorly understood secondary processes associated with trophic dynamics.

INTRODUCTION

Phytoplankton are currently responsible for ~50% of global primary production (Falkowski and Raven, 2007). Climate change over the next century is expected to modify ocean ice cover, temperature, precipitation, and circulation (Meehl *et al.*, 2007), altering the environmental conditions that influence phytoplankton standing stock and primary production (Sarmiento *et al.*, 2004; Irwin and Finkel, 2008). Ocean acidification (Raven *et al.*, 2005a), ozone depletion and associated changes in UV-B in the upper water column (Beardall and Raven, 2004; Beardall and Stojkovic, 2006), coastal eutrophication and other forms of pollution (Ryther and Dunstan, 1971; Fanning, 1989; Smith *et al.*, 1999; Rabalais *et al.*, 2002), along with fishing pressure (Myers and Worm, 2003; Worm *et al.*, 2005) superimpose additional stresses on marine ecosystems. In aggregate, these stressors will modify phytoplankton community structure and have cascading consequences on marine food web dynamics and elemental cycling (Beardall and Raven, 2004;

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Beardall and Stojkovic, 2006). To improve predictions of marine ecosystem responses to environmental and climate change, plankton physiologists and ecologists need to determine how to quantify and parameterize the key physiological responses of plankton that will in turn affect marine food webs and the carbon-climate system.

Model predictions of climate-induced changes in phytoplankton community composition and primary and export production are in their infancy (Anderson, 2005). Current community structure and primary production are predicted typically using simplistic phytoplankton growth models based on nutrient uptake kinetics for a limited number of nutrients, usually some combination of nitrogen, phosphorus, silicon and iron, for a limited number of functional groups of phytoplankton defined using a combination of taxonomy, cell size and biogeochemical function coupled with even more simplistic descriptions of their zooplanktonic predators (Moore *et al.*, 2002; Moore *et al.*, 2004; Hood *et al.*, 2006; Follows *et al.*, 2007). Confidence in these models is limited by a lack of knowledge on several fronts, including data to constrain the choice of physiological parameters that differentiate the functional groups and identify all the biotic and abiotic factors that control primary production and community structure. Many questions need to be addressed, e.g. what environmental factors are limiting? How do these environmental factors interact to influence physiological traits of different functional groups? What functional groups and physiological traits should be included in the models? We lack mechanistic understanding of processes required for the correct structuring of models; in particular, difficulties in reconstructing community structure are compounded by our tenuous understanding of competitive interactions, grazing and loss processes. Construction of detailed physiological profiles of all the many thousands of phytoplankton species is impracticable. A potential way forward is to decrease model complexity by focusing on eco-physiological traits that predict not only phytoplankton growth rates but also elemental cycling and food web dynamics, in response to key environmental variables.

Phytoplankton cell size, elemental requirements and composition are physiological traits that have potential to impose fundamental constraints on the rate of acquiring (Munk and Riley, 1952; Duysens, 1956) and processing energy and materials from the environment (Brown *et al.*, 2004), to influence evolution (Quigg *et al.*, 2003; Bragg and Hyder, 2004; Finkel *et al.*, 2005; Finkel *et al.*, 2007b), food web structure (Laws *et al.*, 2000; Sterner and Elser, 2002; Katz *et al.*, 2004; Irwin *et al.*, 2006) and biogeochemical cycling (Sterner and Elser, 2002; Katz *et al.*, 2004) (Fig. 1). The size structure and elemental composition of phytoplankton communities can alter both the magnitude of carbon fixed and exported into the deep sea relative to the growth-limiting nutrient (Volk and Hoffert, 1985; Falkowski *et al.*, 2000; Laws *et al.*, 2000; Sigman and Boyle, 2000; Armstrong *et al.*, 2002). In this review, we examine how cell size and elemental stoichiometry can inform our understanding of phytoplankton physiology including growth rate, food web structure and biogeochemical cycling of carbon, and therefore improve predictive modelling of phytoplankton community structure. Building on these basic eco-physiological principles, we review the potential effects that environmental changes (i.e. increased atmospheric CO_2, ocean acidification, direct and indirect effects of changes in temperature, including mixed layer depth and nutrient and light regimes in the ocean surface) may have on the cell size and elemental composition of phytoplankton community composition, and what type of information we need to collect in the future to test such hypotheses.

INFLUENCE OF CELL SIZE AND ELEMENTAL STOICHIOMETRY ON PHYTOPLANKTON PHYSIOLOGY, ECOLOGICAL INTERACTIONS AND BIOGEOCHEMISTRY

The eco-physiological characteristics of the species in the phytoplankton community determine the quality (elemental and biochemical composition) and quantity of primary production that is ultimately transferred up the food web and exported to the deep ocean (Fig. 1). The export of photosynthetic products into the deep-ocean and sediment, via the biological pump, takes carbon out of contact with the atmosphere for hundreds to millions of years, influencing atmospheric CO_2 and climate (Volk and Hoffert, 1985). A shift in the phytoplankton size structure from dominance by tiny picoplankton (<2 μm in diameter) to larger nano- and especially micro-phytoplankton is associated with a shift in the pelagic food web away from rapid carbon cycling by the microbial loop dominated by smaller zooplankton, ciliates and flagellates, and bacteria in the ocean surface, to dominance by larger copepods in the zooplankton and an increase in the biological pump due to the more rapid sedimentation of particulate matter (Pomeroy, 1974; Azam *et al.*, 1983; Laws *et al.*, 2000). Shifts in the elemental composition of phytoplankton communities (specifically increases in carbon relative to elements that limit growth, such as N, P, Si and Fe, due either to a direct intra-specific physiological response to growth conditions or changes in species composition with particular elemental signatures, or

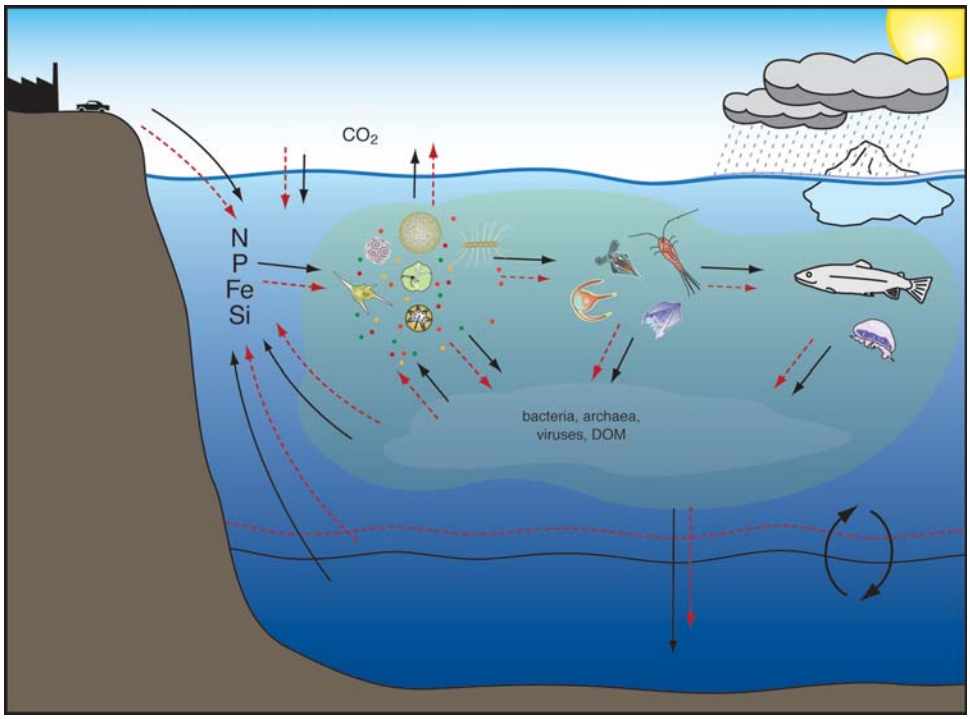

Fig. 1. The interactions between phytoplankton cell size, elemental stoichiometry, marine food webs and biogeochemistry. Changes in pCO_2, the depth of the upper mixed layer and associated changes in nutrient and light regime will regulate the size and taxonomic composition (and therefore elemental stoichiometry) of the phytoplankton community. The size structure and elemental composition of the phytoplankton community has a cascading influence on the proportion of organic material transferred to the microbial loop, higher trophic levels or exported into the deep sea. The magnitude of organic matter exported and buried on the seafloor influences atmospheric CO_2 and climate while the proportion and elemental stoichiomety of the remineralized material influences the quantity and stoichiometry of upwelled nutrient supply for future phytoplankton generations. Fluxes under a warmer, more highly stratified future scenario (red) are contrasted with a cooler, less stratified scenario (black).

both) can increase the amount of carbon exported relative to the amount of limiting nutrient (Falkowski *et al.*, 2000; Sigman and Boyle, 2000). The importance of phytoplankton community structure to the biological pump is poorly understood, and is often a neglected component in carbon-climate research. An improved understanding of how phytoplankton community size structure will respond to climate change is required to improve our understanding of the biological pump and the ability of the ocean to act as a long-term sink for atmospheric carbon-dioxide (Watson and Liss, 1998; Sarmiento and Wofsy, 1999; Kohfeld *et al.*, 2005).

Cell size

Phytoplankton range over nine orders of magnitude in cell volume: from <2 μm in equivalent spherical diameter for the picoplankton, 2–20 μm for the nanoplankton, 20–200 μm for the microplankton, up to 200–$<$2000 μm for macroplankton (Sieburth *et al.*, 1978; Beardall *et al.*, 2009) (Fig. 2). Phytoplankton size affects physiological rates and ecological function, including metabolic rate (growth, photosynthesis, respiration), light absorption (Raven, 1984; Finkel, 2001), nutrient diffusion, uptake and requirements (Pasciak and Gavis, 1974; Shuter, 1978; Aksnes and Egge, 1991; Hein *et al.*, 1995), sinking rate, maximum numeric abundance and grazing rates (Frost, 1972; Kiorboe, 1993; Waite *et al.*, 1997). Quantitative relationships between phytoplankton cell size and physiological and ecological processes (size rules) can be used to construct models of primary production, standing stock and export production. A summary of some of the major physiological and ecological processes that scale with size is provided in Table I. Note there are exceptions to these "size rules" whose importance in terms of biogeochemical and trophic dynamics remain poorly understood.

The origin of many of the size scaling of the patterns processes identified in Table I may be the power-law relationship between maximum metabolic rates (R) and organism size (M):

$$R = a \cdot e^{-Ea/kT} M^b \quad (1)$$

where a is a constant, E_a the activation energy for the metabolic machinery, k the Boltzmann's constant, b the

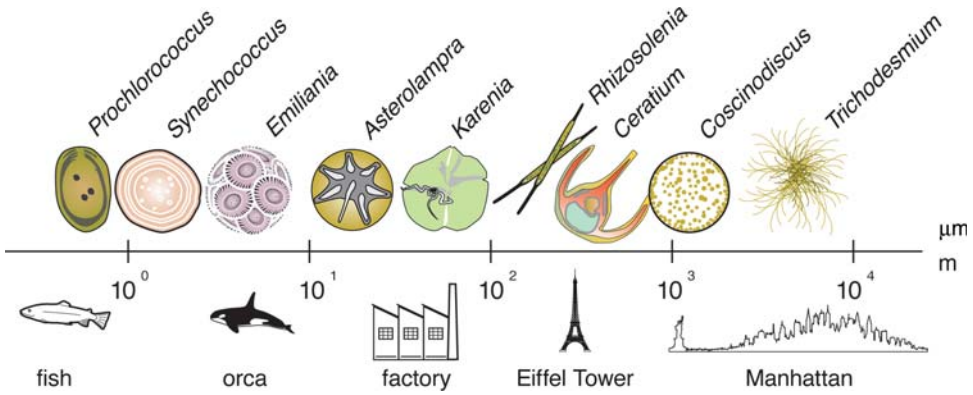

Fig. 2. A comparison of the size range (maximum linear dimension) of phytoplankton relative to macroscopic objects.

Table I: A selection of physiological and ecological processes and parameters that can be expressed as a power-law function of organism size ($\propto aV^b$), where V is cell volume

Physiological rates and ecological patterns	Size-dependence and relationship to other variables
Metabolic rate (time^{-1})	Under optimal environmental conditions, metabolic rates (time^{-1}) often scale with volume with a size scaling exponent $b = -0.25$ (Hemmingsen, 1960; López-Urrutia *et al.*, 2006). This exponent may be due to the scaling properties of intracellular transportation networks (West *et al.*, 1999; Banavar *et al.*, 2002). There appear to be taxonomic differences in the intercept (Moloney and Field, 1989; Tang, 1995; Raven *et al.*, 2006). This exponent and intercept varies under sub-optimal growth conditions due to the size scaling of resource acquisition (Finkel *et al.*, 2004; Irwin *et al.*, 2006; Mei *et al.*, 2009).
Maximum nutrient uptake rate (mol N (cell time) $^{-1}$) and half saturation constant (mol N)	Maximum nutrient uptake rate is a function of surface area and enzymes and transporter concentrations and tends to have a size scaling exponent *b* of ~2/3. The half-saturation constant has a size-scaling exponent *b*~1/3 (Grover, 1989; Aksnes and Egge, 1991; Grover, 1991; Hein *et al.*, 1995; Mei *et al.*, 2009)
Nutrient diffusion (mol N (cell time) $^{-1}$)	Nutrient diffusion rate $\propto 4\pi RD\Delta C$ (*D*, molecular diffusivity; *R*, cell radius, ΔC is the difference in nutrient concentration between the cell surface and bulk medium)
Light absorption (a*, m^2 mg Chl-*a*$^{-1}$)	Light absorption per unit of chlorophyll is a function of cell size and intracellular pigment concentration (Duysens, 1956; Bricaud *et al.*, 1988; Agustí, 1991a; Kirk, 1994). Under light limitation $b = -0.08$. (Finkel, 2001; Finkel *et al.*, 2004)
Cellular composition, mol nutrient or chlorophyll per cell (mol N cell^{-1})	In phytoplankton C, N and P tend to have *b* ranging from 0.7 to 0.9, with some variability between taxonomic groups and elements (Strathmann, 1967; Thompson *et al.*, 1991; Menden-Deuer and Lessard, 2000; Montagnes and Franklin, 2001). There is some evidence that *b* may vary under nutrient saturating versus limiting conditions (Shuter, 1978). A similar relationship may exist for trace metals, but more measurements are needed. The size scaling of cellular chlorophyll varies with irradiance: $b = 2/3$ under light limitation but tends to three fourth under light saturating conditions (Agustí, 1991a; Finkel *et al.*, 2004)
Sinking velocity, particle aggregation	Sinking velocity increases with the size ($b = 2/3$) according to Stoke's law (Denny, 1993). Aggregation increases with cell abundance (Smayda, 1970; Bienfang *et al.*, 1977; Burd and Jackson, 2002), which can result in larger particles
Population abundance (# cells/L)	The numerical abundance of organisms in an area or volume can often, but not always, be approximated as a power law relationship of cell size with $b = -5/3$ to $-2/3$, often -1. The intercept and exponent varies with environmental conditions (Agustí *et al.*, 1987; Agustí, 1991b; Vidal and Duarte, 2000; Boss *et al.*, 2001; Belgrano *et al.*, 2002; Irwin *et al.*, 2006)
Trophic interactions	The body size of the consumer is often correlated with the size of prey consumed; larger predators eat larger prey and a larger range of prey sizes (for review see Woodward *et al.*, 2005)
Diversity	Organism diversity within taxa is often a log-normal distribution of body size; maximum diversity occurs at a size somewhat smaller than the median (Van Valen, 1973; May, 1990; Fenchel, 1993; Cermeño and Figueiras, 2008)

size scaling exponent and *T* the temperature. A three-fourth size-scaling of metabolic rates (constant *b*) under favourable growth conditions has been observed for many organisms from numerous taxonomic groups (Kleiber, 1947; Hemmingsen, 1960; López-Urrutia *et al.*, 2006) and has been attributed to the size-scaling

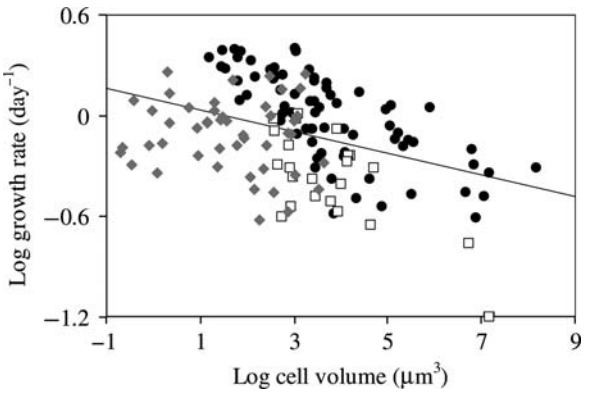

Fig. 3. Size dependence (cell volume, μm^3) of temperature-corrected growth rate (day^{-1}) for diatoms (filled circles), dinoflagellates (open boxes) and other taxonomic groups (grey diamonds, a combination of cyanobacteria, chlorophyte, haptophyte, cryptophyte and various ochrophyte groups). Line is the least-squares regression of all data (log $\mu = -0.06$ log $V + 0.1$; $r^2 = 0.15$). The slope and intercept are affected by the taxonomic composition of the data set and the growth conditions for each species (see text for discussion). Data compiled by T.A.V. Rees.

of transportation networks within organisms (Banavar *et al.*, 2002), but for alternative hypotheses see Dodds *et al.* (2001), Cyr and Walker (2004), and Kozlowski and Konarzewski, (2004). Application of equation (1) implies that >2 orders of magnitude in the maximum growth rate ($time^{-1}$) of phytoplankton can be attributed to cell size.

Studies on the size scaling of phytoplankton growth and other metabolic rates have yielded a wide range of size scaling slopes and intercepts, due in part to the effect of taxonomic differences and environmental conditions on the slope and exponent in equation (1) (Fig. 3) (Banse, 1976; Taguchi, 1976; Schlesinger *et al.*, 1981; Moloney and Field, 1989; Sommer, 1989; Finkel, 2001; Finkel *et al.*, 2004; Mei *et al.*, 2009). Differences in the intercept, *a*, reflect large (over an order of magnitude), well-known size-independent taxonomic differences in metabolic rate (Moloney and Field, 1989; Irwin *et al.*, 2006; Raven *et al.*, 2006); for example, dinoflagellates generally have lower growth rates than diatoms of comparable size (Tang, 1996). Sub-optimal growth temperatures, irradiances and nutrient concentrations can alter both the slope and intercept in equation (1) and likely contribute to often reported variation in the size scaling exponent reported for phytoplankton from multiple laboratory and field studies (Finkel and Irwin, 2000; Finkel, 2001; Gillooly *et al.*, 2001; Finkel *et al.*, 2004; Irwin *et al.*, 2006; López-Urrutia *et al.*, 2006; Marañón, 2008). In addition, when comparing size scaling patterns in phytoplankton to other organisms, the appropriate measurement of organism size and metabolic rate must be considered. There is considerable size-dependence in cellular carbon as a function of cell volume, due to an increase in the proportion of cell volume taken up by vacuoles in larger cells (Sicko-Goad *et al.*, 1984; Raven, 1987; Raven, 1997). These issues are not trivial; the size scaling exponents associated with metabolism will vary depending on what measure of organism size is used and how metabolic rates are measured. Despite these caveats, phytoplankton size is an easily determined and promising trait for predicting physiological responses to environmental change that can be used to scale-up to ecological and biogeochemical processes; often referred to as the metabolic theory of ecology (Brown *et al.*, 2004; López-Urrutia, 2008).

Elemental stoichiometry

Organism size and elemental composition of the phytoplankton community will influence processes at the level of individuals, populations, communities and ecosystems (Sterner and Elser, 2002; Hessen and Elser, 2005). The metabolic rate of a photosynthetic organism is the rate at which it acquires energy and materials (i.e. elements) from the environment and converts that energy and materials into products that it requires for maintenance, growth and reproduction with any necessary carbon loss in respiration and excreted organic and inorganic materials. Metabolic rate is a function of cellular biochemistry, which carries with it a stoichiometric burden in its elemental requirements (Geider and LaRoche, 2002; Elser *et al.*, 2003; Flynn *et al.*, 2009). Conversely, the elemental stoichiometry of an organism can be influenced by both metabolic rate and physical size such as the changes in elemental stoichiometry that occur with increased degree of vacuolation (Raven, 1997; Gillooly *et al.*, 2005; Flynn *et al.*, 2009).

A combination of biochemical, physiological, ecological and evolutionary factors have shaped the elemental stoichiometry of organisms (Geider and LaRoche, 2002; Sterner and Elser, 2002; Quigg *et al.*, 2003). The most widely used stoichiometric relationship reported for marine phytoplankton is the C:N:P ratio, though it can be extended to include other elements such as the trace metals (Ho *et al.*, 2003; Quigg *et al.*, 2003). Healthy natural assemblages of marine plankton often tend to have molar C:N:P ratios of around 106:16:1, referred to as the Redfield ratio since its original description in the 1930s (Redfield, 1934; Falkowski, 2000; Arrigo, 2005). Individual species rarely display the Redfield ratio (Geider and LaRoche, 2002; Ho *et al.*, 2003; Klausmeier *et al.*, 2004) (Table II), and their elemental composition has been shown to vary widely with changes in the concentration of bio-available N and P (Turpin, 1986; Ågren, 2004), and somewhat less so with

Table II: Taxonomic differences in elemental stoichiometry (geometric mean (coefficient of variation))

Taxonomic group	Volume (μm^3)	Elemental stoichiometry C:P (mol:mol)	C:N (mol:mol)	N:P (mol:mol)	Fe:P (mmol:mol)
Cyanobacteria					
Prochlorococcus sp.	10^0	105[a]	6.2[a]	17[a]	
		121 – 215[b]	5.7 – 9.9[b]	15.9 – 24.4[b]	
Synechoccocus sp.	10^0	110[a]	5.8[a]	19[a]	15 (11%)[c]
		113 – 165[b]	5 – 10[b]	13.3 – 33.2[b]	
Nitrogen-fixing cyanobacteria					
Cyanothece sp.	10^0		8.6[d]		6 – 271[d]
			5.9 – 11.37[d]		
Trichodesmium sp.	10^{11}	262 (11%)[c]	7.8 (1.1%)[c]	49 (13%)[c]	48 (54%)[c]
In the field		290[e]	5.5[e]	53[e]	
Various [Fe]					0.8 – 22[d]
Green algae					
Chlorophytes	$10^1 – 10^4$	197 (3.5%) [f]	8.5 (1.2%)[f]	26 (10%)[f]	11 (12.7%)[f]
		28 – 50[g]	5.1 – 7.4[g]	5.3 – 6.8[g]	
Haptophytes	$10^1 – 10^4$	63 (10%)[f]	8.4 (0.2%)[f]	7.2 (22%)[f]	2 (8.1%)[f]
		44 – 128[g]	5.2 – 7.9[g]	5.6 – 18[g]	
Diatoms	$10^2 – 10^{13}$	56 (11%)[f]	8.4 (1.3%)[f]	8.0 (20%)[f]	1.2 (22%)[f]
		35 – 110[g]	5.1 – 9.0[g]	4.9 – 17[g]	
			6.2 – 13.3[h]		
Dinoflagellates	$10^2 – 10^8$	130 (5.5%)[f]	8.1 (2.3%)[f]	9.5 (33%)[f]	2.6 (10.5%)[f]
HAB species		36 – 166[g]	5 – 11.3[g]	5.5 – 23[g]	
		∼105 – 135[i]	∼7 – 7.5[i]	∼16 – 18[i]	

Residual variability is due to differences in growth conditions and finer scale taxonomic variation.
[a]Fu *et al.* (2007).
[b]Bertilsson *et al.* (2003).
[c]Quigg *et al.* (in preparation).
[d]Berman-Frank *et al.* (2007).
[e]White *et al.* (2006).
[f]Quigg *et al.* (2003), excluding *Gymnodinium chlorophorum.*
[g]Leonardos and Geider (2004).
[h]Brzezinski (1985).
[i]Fu *et al.* (2008).

changes in irradiance, temperature and carbon-dioxide (Finkel *et al.*, 2006; Fu *et al.*, 2007; Hutchins *et al.*, 2007; Fu *et al.*, 2008). Similarly, commonality in trace element stoichiometry has been interpreted as a reflection of basic biochemical requirements while differences define unique strategies among taxa that determine their environmental niche (Ho *et al.*, 2003; Quigg *et al.*, 2003; Klausmeier *et al.*, 2004; Arrigo, 2005). There is accumulating evidence that a species' elemental stoichiometry varies with environmental conditions (Cullen and Sherrell, 2005; Finkel *et al.*, 2006; Finkel *et al.*, 2007a). Major taxonomic differences in C:N:P and the trace element Fe are summarized in Table II. These data are preliminary; as such, taxonomic comparisons should be done with organisms growing at the same rate and environmental conditions. More data are required on the relationship between elemental stoichiometry, changes in growth rate and environmental conditions.

Changes in climate may facilitate a shift in the species composition in a manner that can alter the elemental composition of particulate matter, cell size and the trajectory of primary production through the food web, influencing the proportion of the biomass exported to the deep sea (Fig. 1). Changes in the total mass of carbon exported relative to growth-limiting nutrients such as nitrogen, phosphorus and iron can increase the efficiency of the biological pump (Fig. 1). For example, a shift from growth saturating to limiting nitrate and ammonium concentrations under growth saturating concentrations of phosphate can result in a shift from diatoms to nitrogen-fixing cyanobacteria (Karl and Lukas, 1996; Falkowski, 1997; Tyrell, 1999), altering the C:N:P:Fe (and Si) in particulate matter (Table II) and decreasing the magnitude of particulate organic matter exported into the deep sea (Fig. 1). Phenotypic changes in the elemental stoichiometry of phytoplankton taxa to environmental factors such as irradiance, temperature and nutrient concentrations (Finkel *et al.*, 2006; Berman-Frank *et al.*, 2007; Finkel *et al.*, 2007a; Fu *et al.*, 2007; Hutchins *et al.*, 2007; Fu *et al.*, 2008) can be of similar or larger magnitude than changes due to shifts in taxonomic structure (Table II). These changes in the elemental composition of phytoplankton particulate organic matter can in turn influence the success and composition of higher trophic levels. Zooplankton growth is affected by the ratio of carbon to limiting

nutrient in prey (Jones and Flynn, 2005), which varies with the concentration of limiting nutrient as well as environmental conditions such as irradiance and CO_2 (Urabe *et al.*, 2002; Urabe *et al.*, 2003). Consumption of poor-quality prey by zooplankton can result in restricted regeneration of the limiting element and further limit primary production (Mitra and Flynn, 2005; Mitra and Flynn, 2006). Over sufficiently long timescales, the elemental composition of the particulate matter formed by phytoplankton and resulting food web interactions has the potential to influence the concentration and ratios of nutrients upwelled from depth, potentially impacting ecological and evolutionary succession in the phytoplankton (Fig. 1).

PHYTOPLANKTON CELL SIZE AND ELEMENTAL STOICHIOMETRY IN A CHANGING WORLD

In this section, we summarize data collected from laboratory experiments on model organisms, field observations and mathematical models to explore how some current and future anthropogenic changes in the marine environment are likely to alter the size and elemental stoichiometry of phytoplankton communities.

General effects of increased CO_2 on growth rate, elemental composition and organism size

About 48% of the CO_2 released to the atmosphere over the last ca. 200 years as a result of the burning of fossils fuels, manufacturing cement and changing land use has entered the ocean (Raven *et al.*, 2005a). An increasing concentration of CO_2 in surface waters is resulting in slightly higher bicarbonate concentrations, lower carbonate concentrations and a lower pH, altering carbonate and aragonite saturation horizons. Increases in CO_2 might be expected to stimulate growth rate or resource use efficiency, and therefore alter species composition, since Rubisco, for most phytoplankton species examined, is less than half saturated under current CO_2 levels (Giordano *et al.*, 2005). Experiments investigating the impact of increasing inorganic CO_2 on growth have yielded a range of results due to physiological variation between species including differences in carbon concentrating mechanisms and experimental protocols.

Clark and Flynn (2000) examined the inorganic carbon dependence of growth in nine species of marine phytoplankton organisms at constant pH using an inorganic carbon drawdown technique starting from present-day inorganic carbon concentrations and found the half-saturation concentration of inorganic carbon for carbon-specific growth was in the range 30–750 mmol m^{-3}, indicating that additional CO_2 would not increase growth rate (Clark and Flynn, 2000). A technique for increasing CO_2(aq) in seawater is to add mineral acid; however, this method has the drawback of decreasing alkalinity and hence not accurately representing the inorganic carbon speciation and total concentration under increased atmospheric CO_2 (Hurd *et al.*, 2009). This problem could be overcome by addition of appropriate quantities of $NaHCO_3$ (Hurd *et al.*, 2009). An alternative method for altering the CO_2 availability for growth is to bubble cultures with air containing different concentrations of CO_2; this is arguably a better mimic of the real world situation, though some phytoplankton organisms are intolerant of bubbling (e.g. Fu *et al.*, 2007, Riebesell *et al.*, 2007, Feng *et al.*, 2008, Iglesias-Rodriguez *et al.*, 2008). There is also potential for a local enhancement of CO_2(aq), enhancing the partial pressure of CO_2, that could, if directly translated to enhanced CO_2 concentration at the site of Rubisco, yield an artifactual stimulation of photosynthetic rate. While it may be difficult to quantify this stimulation of photosynthesis by the disequilibrium of CO_2(aq), it may occur in nature, from the spatially inhomogeneous production of CO_2 as the inorganic carbon form lost in respiration by heterotrophs in the photic zone.

These complications notwithstanding, experiments using one or other of the methods show some diversity of findings, but for the marine cyanobacteria *Prochlorococcus, Synechococcus, Trichodesmium* (Beardall *et al.*, 2009) and the prymnesiophycean *Emiliania huxleyi*, an increase in POC per cell for cells grown with additional CO_2 is often observed, suggesting that there is greater carbon productivity at higher CO_2 if cell division rate and cell size remain constant. There is some evidence of additional production of extracellular dissolved organic carbon (DOC) during growth under elevated CO_2 (Riebesell *et al.*, 2007). Increasing CO_2 for growth can lead to enhanced rates of uptake of N and P in microalgae (Beardall unpublished data), though the increase in particulate C is usually greater than that in N or P, so the ratio of C:N and C:P is often higher (but not always) in phytoplankton grown with additional CO_2 (e.g. (Fu *et al.*, 2007; Riebesell *et al.*, 2007; Feng *et al.*, 2008; Iglesias-Rodriguez *et al.*, 2008; Beardall *et al.*, 2009). Burkhardt and Riebesell (1997) examined the effects of CO_2 levels on elemental ratios in *Skeletonema costatum* and a range of other marine phytoplankton. Although the trend was for elevated C:N and C:P at post-industrial compared with pre-industrial CO_2 levels, the responses were species-dependent and

many showed little effect at CO_2 concentrations above present day values. Shifts in trace element stoichiometry have also been reported in response to changes in CO_2, including zinc and cadmium (for diatoms only), metals used in carbonic anhydrase (Cullen *et al.*, 1999).

If the uptake of CO_2 is diffusion limited then theory predicts an advantage for small cells under lower concentrations of CO_2 due to the larger surface area per unit volume, supporting more transporters on their surface, and a thinner diffusion boundary layer. An analysis of laboratory work on individual species of phytoplankton found some supporting and some contradictory evidence for the effects predicted by physical theory (Beardall *et al.*, 2009). Data from natural, mixed-species assemblages of marine phytoplankton (Tortell *et al.*, 2002; Paulino *et al.*, 2008) show some increase in the abundance of larger organisms with additional free CO_2(aq), although again the responses from individual species are somewhat equivocal. In the Equatorial Pacific, Tortell *et al.* (2002) found that while total primary productivity and biomass were unaffected by variations in dissolved CO_2 caused by gas bubbling, the high CO_2 (25 mmol m^{-3}) treatment favoured diatoms over the (often colonial) prymnnesiophyte *Phaeocystis*, and vice versa at low CO_2 (3 mmol m^{-3}). Since *Phaeocystis* in that study occurred mainly in the unicellular flagellate stage, this is not necessarily contrary to physical theory. Paulino *et al.* (2008) found that average picophytoplankton cell numbers were not increased in 200 and 300% CO_2 treatments relative to the controls at the present CO_2 level, while cell numbers of (especially) *Emiliania huxleyi* and also of nano-eukaryotes were greater at higher CO_2, causing a small change in the median cell size (Engel *et al.*, 2008) off the coast of Norway. Tortell *et al.* (2008), using phytoplankton from the Ross Sea (Southern Ocean) in seawater exposed to about one-fourth present, twice present, as well as present CO_2 found that elevated CO_2 increased the productivity (carbon fixed per unit time) of the assemblage, and favoured the occurrence of large colonial diatoms as opposed to small-celled diatoms (Tortell *et al.*, 2008). These data from natural assemblages are generally consistent with the effects predicted from considerations of diffusion. Overall, the data and theory suggest that larger phytoplankton are more likely to respond, relative to smaller organisms, to increases in carbon-dioxide but given the diversity of responses more work is required to ascertain how and why natural communities will shift in response to changing CO_2 concentrations and if these changes are due to differences in carbon concentrating mechanisms, relief from diffusion limitation, or other factors.

There is some evidence that phytoplankton may adapt to changes in CO_2 concentrations and environmental conditions that vary with climate. Over geological timescales (last 65 million years), the diatoms (Finkel *et al.*, 2005), cyst-forming dinoflagellates (Finkel *et al.*, 2007b) and coccolithophores (Henderiks, 2008; Henderiks and Pagani, 2008) all exhibit macroevolutionary decreases in mean cell size consistent with decreases in carbon-dioxide or other limiting nutrient. Recent laboratory studies on *Chlamydomonas* indicate that evolutionary adaptations to changes in CO_2 concentrations, pH and other factors over the year-to-decade scale are possible (Collins and Bell, 2004). Clearly, more studies on long-term exposures to elevated CO_2 and decreased pH are needed to determine the true impacts on phytoplankton growth in a high-CO_2 world.

Calcification and other areas requiring further research

The view that there was a decrease in calcification [accumulation of particulate inorganic carbon (PIC)] by coccolithophores grown with additional CO_2 relative to present-day CO_2 (Raven *et al.*, 2005a) is undergoing revision in the light of more recent data using a greater range of organisms (Lange *et al.*, 2006) and different methodologies (Iglesias-Rodriguez *et al.*, 2008). There is clearly a need for further experimentation using several strains of coccolithophores and a variety of the techniques for changing dissolved CO_2 (Dickson *et al.*, 2007; Langer *et al.*, 2009). However, we may tentatively conclude that the experiments show that the rate of PIC accumulation ranges from being proportional to the excess of calcite saturation over the value at equilibrium with calcite, to essentially invariant with respect to calcite saturation (since calcification is internal in coccolith-forming vesicles). There is concern that increasing ocean acidification (decreasing carbonate) will inhibit calcification and result in reduced abundance of calcifying organism such as the coccolithophorids, corals and pteropods, especially in high latitude regions (Riebesell *et al.*, 2000; Raven *et al.*, 2005a; Orr *et al.*, 2005), although a recent experiment reports an increase in coccolith mass in *Emiliania huxleyi* with increasing CO_2 and a 40% increase in coccolith mass over the last 220 years from an ocean core (Iglesias-Rodriguez *et al.*, 2008).

The effect of decreased pH on the growth of marine phytoplankton as a result of increased CO_2, other that that exerted by increased concentration and changed speciation of DIC and other elements, is not obvious (Hinga, 2002). Experimental evidence indicates species-specific shifts in growth rate (Middelboe and

Hansen, 2007; Nielsen *et al.*, 2007) and suggests that more work is required to determine the effect of pH on marine phytoplankton community structure. At present, the impacts of increased CO_2 on photosynthesis, growth and calcification are unresolved and the complications mentioned above mean that a lot more investigation is needed. In addition to the above reported effects of additional CO_2 on cell composition and growth rate, there are effects of other environmental conditions on the affinity for inorganic carbon of phytoplankton cells in terms of growth (Clark and Flynn, 2000) and photosynthesis (Giordano *et al.*, 2005; Raven *et al.*, 2005b; Raven *et al.*, 2008). These effects are likely to be important as atmospheric CO_2 increases, especially since associated warming will decrease the depth of the upper mixed layer with consequences for the mean PAR incident on the phytoplankton and on the quantity of nutrients trapped in the upper mixed layer when seasonal thermoclines are established (Cyr and Cyr, 2003; Finkel *et al.*, 2007b; Winder and Hunter, 2008).

Temperature: direct and indirect effects

Phytoplankton exhibit an increase in enzymatic reaction rates and growth rates over a moderate range of temperature increase with an average $Q_{10} = 1.88$ (Eppley, 1972). As a result, an increase from 18°C today to 21.5°C could cause an increase of ~25% in growth rate assuming no other factors are limiting. Critically, this also assumes that the taxonomic and indeed clonal composition remains unchanged. The actual effect of temperature on metabolic rate is complicated by species-specific or ecotype-specific temperature ranges and optima for growth, as demonstrated in ecotypes of *Prochlorococcus* (Zinser *et al.*, 2007). Beyond the temperature optima, an increase in temperature can cause cellular damage, inhibition of growth rate and eventually cell death. Based on current data, broad phylogenetic generalizations are extremely uncertain but many dinoflagellate species appear to prefer warmer temperatures, which may be a reflection of mixotrophy and the influence of temperature on heterotrophic metabolism or flagellar motility, while diatoms appear to dominate in temperate to cooler regimes. These patterns may be due to correlated secondary factors such as stratification, light and nutrient availability. Much more data are required to clarify the physiological bases for the species-specific temperature optima and the differences between species and taxonomic groups and the actual relevance to community structure.

The metabolic response of marine species from all trophic levels to changes in average and extremes in ocean temperature could alter phytoplankton communities (Eppley, 1972; Moisan *et al.*, 2002; Edwards and Richardson, 2004). An increase in phytoplankton communities dominated by small picoplankton species has been associated with increases in ocean stratification and the expansion of the ocean gyres (Behrenfeld *et al.*, 2006; Irwin and Oliver, 2009). Shifts in the geographic ranges and the timing of maximum abundance of a number of eukaryotic phytoplankton, zooplankton and marine invertebrates and fish have been detected over the last several decades (Barry *et al.*, 1995; Edwards and Richardson, 2004; Richardson and Schoeman, 2005; Field *et al.*, 2006; Richardson, 2008). There appear to be differences in the effect of changes in temperature on species from different trophic levels; this could alter phytoplankton species composition and the timing of blooms (Rose and Caron, 2007), and could be catastrophic for higher trophic levels that may be cued to environmental factors other than temperature (Edwards and Richardson, 2004). Although these changes are highly correlated with shifts in temperature, it is unclear whether these shifts are due to a direct metabolic response to changes in ocean temperature or indirectly due to changes in light and nutrients and other abiotic or biotic factors associated with changes in ocean circulation and climate (see sections below). Such shifts in community structure, superimposed on intra-specific responses (see section below) may alter the elemental composition of particulate matter (Table II). Other direct effects of temperature include a ~2.5% intra-specific decrease in cell volume with each 1°C increase in temperature (Atkinson *et al.*, 2003). Possible evolutionary causes for cell size decrease include adaptation to decreased oxygen, CO_2 or other nutrient concentrations associated with increasing temperature, or decreases in cell size associated with faster generation times (Atkinson *et al.*, 2003), although for some large bacteria increases in cell size have been associated with increases in growth rate (Schulz and Jorgensen, 2001).

There are known differential effects of temperature on phytoplankton biochemistry, notably for N-assimilation (Lomas and Gilbert, 1999b; Lomas and Gilbert, 1999a). Recent experiments on the raphidophyte *Heterosigma akashiwo*, the dinoflagellate *Prorocentrum minimum* and the cyanobacteria *Trichodesmium*, *Synechococcus* and *Prochlorococcus* indicate that temperature in the range expected with climate change over the next century may have negligible to minor phenotypic effects on C:N:P (Fu *et al.*, 2007; Hutchins *et al.*, 2007; Fu *et al.*, 2008). The combined effect of nutrient, CO_2 concentration and temperature often has a significantly different effect in magnitude and sign on particulate C:N:P than any of the factors individually. Furthermore, changes in community composition and associated differences in elemental composition may be more important that intra-specific changes in

elemental composition in response to temperature. Evidently, temperature will exert profound effects related to both metabolic processes and physico-chemical interactions between phytoplankton cells and the environment. Such effects have clear interactions with cell size. These results and those from other multi-factorial and field experiments need to be compared and the capabilities of current models tested (Flynn, 2001; Flynn, 2003; Litchman *et al.*, 2006) to test our mechanistic understanding.

Effects of the temperature dependence of physical properties of the medium

McNeil and Matear (2006) have modelled an increase in mean sea-surface temperature (SST) from 18°C today to 21.5°C at 2100 AD, with a corresponding freshening of sea-surface salinity (g salt per kg seawater) from 34.71 to 34.53, presumably as a result of increased precipitation and ice melt offsetting increased evaporation from the surface ocean. In considering the potential impacts of a temperature increase of 3.5°C and a salinity decrease of 0.18, we use temperature effects on metabolic processes (enzymic, transmembrane transport), uncatalysed reactions and diffusion from Table I of Raven and Geider (1988); other values come from Denny (1993).

Stokes' law (Denny, 1993) describes the speed at which spherical, non-motile cells move down (cells denser than the surrounding water) or up (cells less dense that the surrounding water) in the water column as a result of density differences. Considering first sinking and flotation unaided by flagellar activity, the terminal velocity for a spherical organism is directly proportional to the density difference, inversely proportional to the dynamic viscosity and proportional to the square of the radius of the organism (Table I). The dynamic viscosity of seawater at 21.5°C is 4.4% lower than the value at 18°C, so other things being equal an organism will move vertically 4.4% faster at 21.5°C than at 18°C. This is equivalent to the increase in speed found for a 2.2% increase in cell radius. For flagellar motility, the force needed to propel a spherical organism at a given speed is directly proportional to the cell radius and to the viscosity of the medium. With a 4.4% decrease in viscosity between 18 and 21.5°C, there would be a pro rata decrease in the energy cost of motility, equivalent to a decrease in the radius of the organism of 4.4%.

The density differences for seawater between 18 and 21.5°C of 1 kg m^{-3} is a result not just of the temperature increase but also of the decrease in salinity. Assuming a density difference of 5 kg m^{-3} between the cells and the medium at 18° C, and the same cell density at 18 and 21.5°C, there would be a 20% increase in the rate of sinking or flotation. This is equivalent to a decrease in cell radius of 4.5%. The assumption of a cell density that is independent of temperature is perhaps unrealistic; a decrease in overall cell density based on a decreased density of the aqueous phase of the protoplast would be more reasonable, so the 20% increase in the rate of vertical motion could be an over-estimate.

A further influence of temperature is on metabolism relative to diffusion through the boundary layer around the organism in relation to the acquisition and assimilation of nutrients, including inorganic carbon, when their rate of supply is limiting for growth (Raven and Geider, 1988; Beardall *et al.*, 2009). Here we use the formalism of control coefficients [Burns *et al.*, (1985) gives terminology and references] which expresses the extent to which a given reaction restricts the rate of a reaction sequence as a decimal fraction, with the sum of control coefficients of all the rate-determining processes equal to 1.0. If we assume an activation energy (E_a) of 60 kJ per mol (Q_{10} of 2) for transmembrane transport and of metabolism, and an E_a of 19 kJ per mol ($Q_{10} = 1.3$) for diffusion through the boundary layer, and a control coefficient of diffusion and of transmembrane transport and metabolism of 0.5 at 18°C, then the control coefficients are 0.46 and 0.54, respectively, at 21.5°C. To re-establish equal control coefficients at 18°C requires a decrease in the boundary layer diffusion restriction to 0.86 at 21.5°C. For organisms with a radius <50 μm where the diffusion boundary layer is numerically equal to the radius, this could be achieved by decreasing the radius by 14%.

Change in ocean circulation, impact on light and nutrient regimes

Coupled ocean atmosphere models project there will be changes in ocean circulation and water column stratification (Sarmiento *et al.*, 1998) and therefore light and nutrient regimes over the next decades due to changes in climate. At present, it is extremely difficult to predict regional or global changes in light and nutrient regimes, as they are not only a function of ocean physics but of phytoplankton growth, standing stock and export. Below we outline the physiological bases for how future changes in light and nutrient regime may affect the size and elemental stoichiometry of phytoplankton communities.

UV and PAR

In high latitude regions, light can limit the growth of phytoplankton due to short winter photoperiods, ice cover and deep surface-mixed layers. Climate warming

will likely result in a transient increase in icebergs, decrease in ice cover in the sea and a decrease in salinity at the poles, which will alter circulation, water column stratification and mixed layer depths. In temperate regions, the spring time warming of surface waters and shallowing of the surface mixed layer often triggers the spring bloom (Sverdrup, 1953). In contrast, in some low latitude regions, shallow-mixed layers can result in cellular damage and inhibited rates of photosynthesis and growth due to high light and increased UV penetration. Increased vertical stratification and shallowing of the mixed layer in these regions may be expected to select species less susceptible to photodamage, with higher rates of repair, and/or other strategies to deal with high light stress such as the production of the antioxidants DMS and DMSP (Sunda *et al.*, 2002) that may act as cloud condensation nuclei (Charlson *et al.*, 1987). Phytoplankton cell size and phylogenetic differences in photophysiological strategies suggest that shifts in light regime due to climate warming will alter phytoplankton community size structure and elemental composition (MacIntyre *et al.*, 2000; Beardall and Raven, 2004; Six *et al.*, 2007). Field and laboratory work indicate there are taxonomic and cell size-related differences in the susceptibility of photosystem II to photoinactivation and in rates of repair (Karentz *et al.*, 1991; Laurion and Vincent, 1998; Quigg and Beardall, 2003; Key *et al.*, 2009; Finkel *et al.*, 2009).

Being small is often beneficial in a light-limiting environment, as internal light shading is lessened; absorption efficiency is higher than in larger cells with the same pigment concentration beyond a threshold pigment concentration. The same argument works the other way when considering the damaging effects of photosynthetically active radiation (Key *et al.*, 2009) and UV radiation (Raven, 1991). All light is damaging, and the capture of photosynthetically active radiation also causes damage to the D1 protein, central to Photosystem II. Small cells are more efficient targets for photoinhibitory radiation and must invest relatively more cellular resources for effective concentrations of UV absorbing compounds than do larger cells, and may be unable to accumulate sufficient UV-absorbing compounds to shield UV-sensitive cellular components (Raven, 1991; Garcia- Pichel, 1994). In general, small species have larger effective cross-sections for photochemistry, and fast metabolic repair of Photosystem II after photoinactivation, while larger cells have lower susceptibility to photoinactivation, and therefore incur lower costs to endure short-term exposures to high light, especially under conditions that limit metabolic rates (Key *et al.*, 2009). Both the repair of D1 and of UV-damaged structures requires a healthy cell metabolism. A cell that is replete with respect to its nutritional demands is best equipped to both continue fixing carbon and to repair UV-induced damage. Interestingly, however, growth of the diatom *Thalassiosira pseudonana* at high CO_2 increases sensitivity to UV-B, although this increased sensitivity is partly offset by prior growth in the presence of UV-B rather than under the normal UV-B-free laboratory culture conditions (Sobrino *et al.*, 2008).

Temperature is also expected to impact phytoplankton physiological responses to irradiance; cells may increase their light-harvesting pigment content to match the rate of downstream thermochemical reactions. This increase in intracellular pigment concentration can increase the package effect (Kirk, 1994; Beardall *et al.*, 2009). This effect can be offset by decreasing the radius of the organism; this effect is very size-dependent, but can be of the order of 10% (Raven, 1984). More work is needed to determine how these interactions will alter the success of organisms of different sizes and taxonomic groups in a warmer world.

Nutrients

Cell size acts as a biophysical constraint on nutrient diffusion and the nutrient requirements of phytoplankton cells (Table I). Nutrient concentration and supply in the upper layers of the ocean are often the primary control on the size and taxonomic structure of phytoplankton communities (Eppley and Peterson, 1979; Chisholm, 1992; Coale *et al.*, 1996). Over vast regions of the ocean available, iron, nitrogen and/or phosphorus concentrations are often too low to support the minimum nutrient requirements of some of the larger phytoplankton species, while Si concentrations often limit diatom growth. Model forecasts predict an expansion of surface ocean stratification in time and space with ocean warming and freshening, which would act to decrease nutrient supply to the surface. Satellite and field observations indicate an increase in the area of the ocean gyres, the degree of stratification of the water column (Behrenfeld *et al.*, 2006; Irwin and Oliver, 2009), which should result in an increase in the proportion of phytoplankton communities dominated by picoplankton (Li, 2002; Irwin *et al.*, 2006; Raven *et al.*, 2006). There is some concern that this shift towards a dominance of small-celled phytoplankton communities will be one of the dominant responses to century-scale climatic change. The fossil record of marine dinoflagellate cysts and diatom frustules over the last 65 million years (Finkel *et al.*, 2005; Finkel *et al.*, 2007b), and diatoms from Lake Tahoe over the last few decades (Winder *et al.*, 2009), document a decrease in the median size of species in the community with water column stratification, suggesting a decrease in

magnitude and variability of nutrient inputs into the surface ocean may act as a downward selective factor on phytoplankton cell size. A shift towards smaller phytoplankton species will have a cascading negative effect on the productivity and size structure of the pelagic and benthic food web and magnitude of carbon export to the deep (Pomeroy, 1974; Smith *et al.*, 1997; Finkel, 2007).

While the ocean's deserts are expanding, there may be a greening of coastal regions due to an increasing temperature gradient between land and sea, causing intensification in upwelling, in conjunction with higher nutrient loads from terrestrial sources (Bakun, 1990; Rabalais *et al.*, 2002; Schlesinger, 2009), an intensification of storm driven upwelling (Black and Dickey, 2008) and nutrient hotspots from ice melt (Smith *et al.*, 2007). Upwelling regions account for less than 1% of ocean area, but stimulate ~20% of the fish yield (Pauly and Christensen, 2002). It has been hypothesized that increased warming will result in intensification of the continental thermal lows adjacent to upwelling regions and this should increase the onshore–offshore atmospheric pressure gradient and alongshore winds and coastal upwelling (Bakun, 1990; McGregor *et al.*, 2007). Cooling of the ocean surface due to the enhanced upwelling and shifts in vegetation type and cover could further alter the land and the thermal contrast between the land and sea (Diffenbaugh *et al.*, 2004). Geological and regional models provide some evidence for enhanced upwelling intensity in response to climate warming, but general circulation models are not currently able to simulate the effect (Diffenbaugh *et al.*, 2004; McGregor *et al.*, 2007). The effect of enhanced upwelling due to increased magnitude and intensity of storms on phytoplankton community structure has also not yet been fully assessed (Black and Dickey, 2008). It seems likely that shifts in phytoplankton community composition under enhanced upwelling and storm magnitude or frequency (Emanuel, 2005; Webster *et al.*, 2005) may be similar to changes observed in mesoscale eddies with increased nutrient availability in the surface; resulting in increases in standing stock biomass, rates of primary production, with an associated increase in the mean cell size of the phytoplankton (McGillicuddy *et al.*, 1998; Williams and Follows, 1998; Sweeney *et al.*, 2003). Ice melt at the poles alters salinity and water column stability, and can act as a source of nutrients (Fig. 1). For example, free drifting icebergs in Antarctica appear to be sources of terrestrial Fe, stimulating high chlorophyll biomass and diatom growth in some regions (Smith *et al.*, 2007). Decreased salinity affects phytoplankton physiology through altering the synthesis of osmoticums; laboratory cultured species often grow faster at lower salinity (ca. salinity of 25 rather than 30+). Much additional research is required to estimate of the impact of ice melt and icebergs on primary and export production, community structure and elemental composition.

CONCLUSIONS AND FUTURE DIRECTIONS

On the decadal scale, there is already clear evidence of increases in ocean temperature, decreases in ocean pH, strengthening in the westerly winds (Meehl *et al.*, 2007), a decrease in summer sea ice in the high latitudes (Curran *et al.*, 2003; Serreze *et al.*, 2007), an increase in salinity in low-latitude waters, an increase in the magnitude and intensity of certain types of storms in some regions (Goldenberg *et al.*, 2001; Emanuel, 2005) and expansion of the ocean gyres (Behrenfeld *et al.*, 2006; Polovina *et al.*, 2008; Irwin and Oliver, 2009).

One way to predict the impact of these changes on phytoplankton community structure over the next decades is to model growth and loss processes under the changing environmental conditions using the eco-physiological differences between species. Cell size and elemental stoichiometry both appear as potential eco-physiological traits to use in such a model framework. These traits fundamentally link growth rate, nutrient and light harvesting capabilities, influence loss processes such as sinking, grazing susceptibility and food web dynamics, as well as biogeochemical cycling. However, it is clear that while there are sound reasons to expect these traits to be affected in one or other direction, there are more than enough exceptions to these rules to indicate that we must tread very carefully.

Based on general circulation model projections and a current assessment of the basic eco-physiological response of phytoplankton it seems likely that the expanding low productivity, highly stratified regions will continue to be dominated by picoplanktonic prokaryotic and eukaryotic genera. Stratification caused by glacial ice melt in polar regions will likely continue to cause shifts in phytoplankton community composition from diatoms to small phytoplankton cells (in this case often Cryptophytes), and consequently from krill to salps, altering higher trophic levels and elemental cycling (Moline and Prezelin, 1996; Montes-Hugo *et al.*, 2009). However, there is no certainty that such a path will in fact be played out. For example, the abundance of cryptophytes can stimulate mixotrophic growth (Adolf *et al.*, 2008), and the activity of these organisms can lead to an upgrading of seston food quality by altering its stoichiometric content (Ptacnik *et al.*, 2004).

Macroevolutionary trajectories in the size of diatoms and dinoflagellates over the Cenozoic are consistent with

a shift towards smaller cells in a more stratified ocean (Finkel *et al.*, 2005; Finkel *et al.*, 2007b). The impact of these shifts in taxonomic composition will potentially alter the elemental composition of primary production, as could temperature induced changes the rate of bacterial remineralization of different nutrients (Bidle *et al.*, 2002). Increases in coastal upwelling and storms could increase nutrient availability in the surface and may select for larger taxa, such as diatoms (Babin *et al.*, 2004) in some temporally and spatially localized regions of the ocean. Temperature stimulated increases in metabolic rate (in the absence of nutrient limitation) and growing season in temperate and high latitude regions, and increases in the supply of iron and silicate dust to the ocean, also have the potential to increase primary and export production (Sarmiento *et al.*, 2004), support larger phytoplankton taxa and shift particulate elemental stoichiometry. In addition, temporal and spatial changes in the geographic distribution phytoplankton taxa, in relation to one another, and other trophic levels, are likely to shape community structure through shifts in competitive interactions and loss processes due to grazing, parasitoid and viral pressures (Harvell *et al.*, 1999; Edwards and Richardson, 2004; Richardson and Schoeman, 2005; Rose and Caron, 2007; Richardson, 2008).

More research to determine how growth rate, cell size and elemental composition is affected by the suite of changing environmental conditions expected under climate change will help improve the framework to incorporate phytotoplankton growth and community structure, as well as higher trophic levels, into general circulation models to improve predictions of the impact of climate change on marine food web structure. It is likely that the taxonomic changes in phytoplanktonic prey items for zooplankton, and indeed in the direct temperature affects upon zooplankton selection, are likely to have equally profound impacts upon plankton community structure and carbon export. The issues raised here demonstrate the breadth of work required upon the phytoplankton before we can enhance our predictive capabilities.

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