

Representations of biological calcification in two climate models

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Publication Date:

2014

DOI:

<https://doi.org/10.26190/unsworks/17208>

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Representations of biological calcification in two climate models

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A thesis in fulfilment of the requirements for the degree of
Doctor of Philosophy

CLIMATE CHANGE RESEARCH CENTRE
SCHOOL OF BIOLOGICAL, EARTH AND ENVIRONMENTAL
SCIENCES

FACULTY OF SCIENCE

December 2014

Abstract

Present and future changes to the ocean organic carbon and carbonate pumps are and will continue to affect ocean ecosystem dynamics and biogeochemical cycles. In this thesis, the ocean organic and carbonate cycles are modelled with a variety of parameterisations and complexity and used to simulate both pre-industrial as well as future hypothetical states. The models produce similar pre-industrial states but very different transient behaviours. A simplistic Biogeochemistry-Ocean Model, the CSIRO-Mk3L, demonstrates a large future ocean saturation state sensitivity to enhanced organic carbon export and reduced carbonate export, though sedimentary carbonate compensation is not considered. A more complex Earth System Model, the University of Victoria Earth System Climate Model (UVic ESCM), is improved with the inclusion of a calcifying phytoplankton functional type, a full calcite tracer, carbonate chemistry dependent calcite dissolution rates, and a ballasting scheme. These modifications slightly improve UVic ESCM performance with respect to observed carbon and nutrient fluxes and greatly improve the mechanistic realism of the model. Addition of a carbonate chemistry dependency on calcifier microbial recycling rates improves calcifier biogeography, but produces mixed results with respect to observed carbon and nutrient fluxes. Greenhouse gas forcing of four variations of the UVic ESCM (1: without calcifiers, 2: with calcifiers, 3: with calcifiers and prognostic CaCO_3 , and 4: with calcifiers, prognostic CaCO_3 , and chemistry-dependent calcifier microbial recycling) show a common response of a transition between two globally dominant biogeochemical feedbacks. The first is a physically driven one that dominates at lower changes in sea surface temperatures (SSTs) and is sensitive to phytoplankton community composition. The second dominant feedback is biologically driven and overtakes the first at higher SST changes. The deep ocean carbon export and oxygen response is found to be highly sensitive to the inclusion of a prognostic calcite tracer for higher SST changes under this second dominant feedback. This thesis underscores the importance of accurate representation of phytoplankton physiology and ecology in climate models, as well as inclusion of prognostic calcite that accounts for organic carbon ballasting. It also highlights the potentially underappreciated role of microbial processes under both ocean warming and acidification.

Originality Statement

‘I hereby declare that this submission is my own work and to the best of my knowledge it contains no materials previously published or written by another person, or substantial proportions of material which have been accepted for the award of any other degree or diploma at UNSW or any other educational institution, except where due acknowledgement is made in the thesis. Any contribution made to the research by others, with whom I have worked at UNSW or elsewhere, is explicitly acknowledged in the thesis. I also declare that the intellectual content of this thesis is the product of my own work, except to the extent that assistance from others in the project’s design and conception or in style, presentation and linguistic expression is acknowledged.’

Relevant Publications and Presentations

Publications and presentations have arisen over the course of writing this thesis. Full citations for the manuscripts can be found in the bibliography.

Publications:

Kvale KF et al. (2014). Explicit planktic calcifiers in the University of Victoria Earth System Climate Model version 2.9, Atmosphere-Oceans, in review.

Kvale KF et al. (2011). The combined impact of CO₂ - dependent parameterizations of Redfield and rain ratios on ocean carbonate saturation. Biogeosciences Discussions.

Presentations:

Explicit planktic calcifiers in the UVic ESCM, American Geophysical Union Ocean Sciences Meeting. Salt Lake City, USA, 02/23/2012.

Adding calcifiers to the UVic Model, SOLAS Summer School. Corsica, France, 08/2011.

The combined impact of CO₂-dependent parameterizations of Redfield and rain ratios on ocean carbon chemistry, American Society of Limnology and Oceanography Aquatic Sciences Meeting. San Juan, Puerto Rico, 02/17/2011.

Acknowledgements

This thesis was supported by an award under the Merit Allocation Scheme on the NCI National Facility at the ANU, as well as by UNSW through a University International Postgraduate Award, and the ARC Centre of Excellence for Climate System Science.

The author would like to thank Assoc. Prof. Katrin Meissner and Prof. Andy Pitman, both of whom went beyond their regular duties to ensure she was supported through the sometimes difficult circumstances of her tenure. Dr. Meissner's thesis supervision at times included roles as cheerleader, bulldog, baby sitter, swim instructor, slave driver, chef, fashion advisor, fortune teller, life coach and friend, for which the author is grateful.

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Nomenclature

Ω	Calcium carbonate saturation state
<i>E. huxleyi</i>	Common coccolithophore <i>Emiliana huxleyi</i>
CaCO ₃	Particulate calcium carbonate
CMIP5	Coupled Model Intercomparison Project phase 5
DIC	Dissolved Inorganic Carbon
DMS	Dimethyl Sulphide
DOC	Dissolved Organic Carbon
EMIC	Earth Models of Intermediate Complexity
EP	Export Production; POC and CaCO ₃ production and export from the near-surface
GLODAP	Global Data Analysis Project
Mk3L	CSIRO-Mk3L coarse resolution climate model
NPP	Net Primary Production
NPZD	Nutrients Phytoplankton Zooplankton Detritus
OCMIP	Ocean Carbon-Cycle Model Intercomparison Project
OGCM	Ocean General Circulation Model
PFT	Plankton Functional Type
POC	Particulate Organic Carbon
POP	Particulate Organic Phosphate
Rain Ratio	CaCO ₃ :POC production ratio
RCP	Representative Concentration Pathways
SST	Sea Surface Temperature

TA Total Alkalinity

UVic ESCM University of Victoria Earth System Climate Model

WOA World Ocean Atlas

Chapter 1

Introduction

Earth system models are incorporating ever larger ecological schemata to represent our growing mechanistic understanding of biological connections to global biogeochemical cycles. In the ocean, “Dynamic Green Ocean Models” (Le Quéré et al., 2005) use multiple plankton functional types (PFTs) to explicitly link marine organisms to global chemical cycles through ecology and physiology. PFTs are not explicit organisms, but are instead conceptual classifications of marine plankton according to their biogeochemical role (Hood et al., 2006).

1.1 Pelagic Calcifiers and the Marine Carbon Cycle

Pelagic calcifiers as a PFT (phytoplankton coccolithophores, and zooplankton foraminifera and pteropods) are responsible for over half of the global calcium carbonate production (Milliman, 1993), with 59–77% of this production from coccolithophores (Fabry, 1989), 23–56% from foraminifera (Schiebel, 2002), and 4–13% from pteropods (Fabry, 1989). Biogenic calcification (Equation 1.1) forms particulate calcium carbonate (CaCO_3), which accounts for about 4% of the global annual carbon export out of the euphotic zone (Jin et al., 2006, , and Figure 1.1). Global annual export fluxes of CaCO_3 amount to about 1.14 Pg C per year (Jin et al., 2006).



A 34% global average calcium carbonate composition in marine sediments (Archer, 1996a), however, indicates that biogenic CaCO_3 is an important vector for long-term, open ocean carbon sequestration. Furthermore, CaCO_3 exporting from the surface ocean might act as a globally significant ballast for particulate organic carbon (POC, Armstrong et al., 2002), a phenomenon responsible for 80–83% of the POC

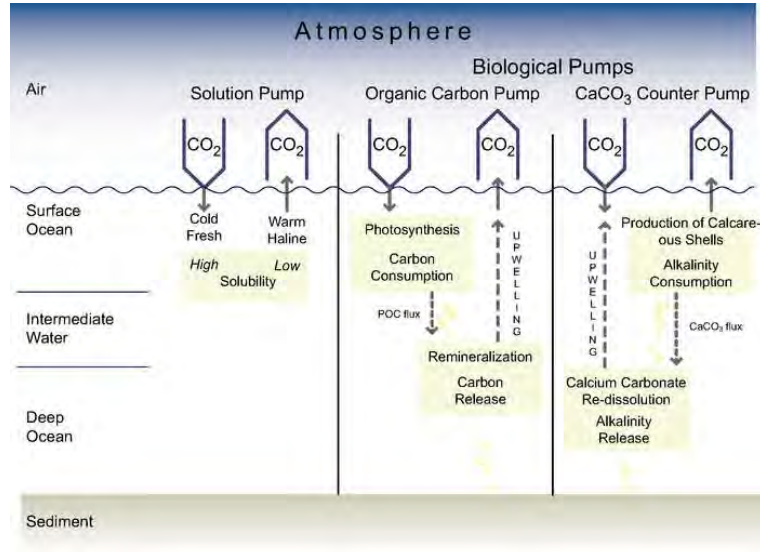


Figure 1.1: Marine carbon cycle schematic from Heinze et al. (1991).

that ends up in the benthos (Klaas and Archer, 2002), though the presence of a simple physical mechanism has recently been called into question due to a lack of spatial correlation between CaCO_3 and POC (Wilson et al., 2012).

Pelagic calcifiers not only contribute to deep sea and benthic carbon inventory, but also affect the atmosphere-ocean CO_2 gradient through the release of CO_2 during calcification (Equation 1.1, Zondervan et al., 2001, , and Figure 1.1). This release of CO_2 provides a chemical link between calcification and photosynthesis (Equation 1.2 and Figure 1.1), where some of it is used for POC production. Global annual export fluxes of POC amount to about 9.8 Pg C per year (Jin et al., 2006).



Phytoplankton coccolithophores participate in the production and export of both CaCO_3 and POC. Calcifying zooplankton fecal material is a combination of CaCO_3 and POC as a result of their diet, and is an effective transport mechanism for POC to the deep ocean (summarised by Le Quéré et al., 2005).

1.2 Calcifier Characteristics

1.2.1 Coccolithophores

Roughly 200 coccolithophore species live in the modern global ocean (Winter and Siesser, 1994). Of these, *Emiliania huxleyi* has been studied most extensively. The

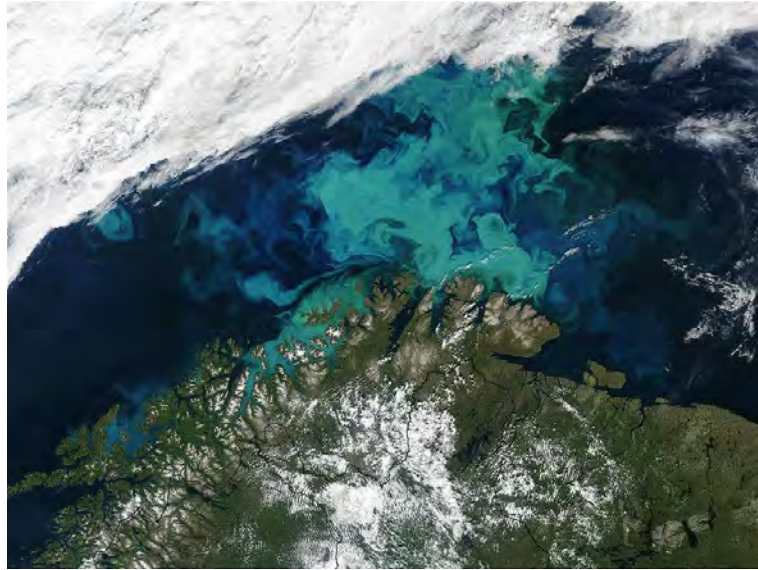


Figure 1.2: Satellite image of an *E. hux* bloom in the Barents Sea (NASA, 2013).

reasons are partly historical; Westbroek et al. (1993) called for experimental and modelling work to focus on this single representative species as a first step towards constraining the role of all coccolithophores in the global carbon cycle and their role in dimethyl sulphide (DMS) production. The reasons are also partly practical; *E. huxleyi* is one of only a few coccolithophore species that form blooms observable by satellites (Figure 1.2), it is widely distributed and composes 20–50% of the coccolithophore community over most of the global ocean, and it is easy to grow and study in controlled laboratory or mesocosm conditions (summarised by Westbroek et al., 1993). Tuning calcification in models to *E. huxleyi* introduces two major biases; the first being that the role of the species is overstated and significantly under-estimates the CaCO_3 export contribution from non-bloom forming species (Sarmiento et al., 2002). The second major bias is that *E. huxleyi* is not physiologically representative of extinct but formerly abundant coccolithophore species (which were generally more massive), and tuning to the species biases the model to the modern ocean, hampering our efforts to understand rapid warming events like the Paleocene-Eocene Thermal Maximum.

Satellite reconstructions of CaCO_3 concentration in the euphotic zone show strong seasonal and regional variability (Balch et al., 2005). A recent data compilation by O’Brien et al. (2013) shows coccolithophore presence and abundance peaks around 20°S and 60°N. Much of the seasonal variability comes in the form of high latitude summer calcifier blooms, where about 69% of the October to March

global CaCO_3 concentration occurs in the Southern Hemisphere (40% south of 30°S), and 59% of the April through September global CaCO_3 concentration occurs in the Northern Hemisphere (29% north of 30°N ; Balch et al., 2005). These blooms can be extensive and have been observed to exceed $100,000 \text{ km}^2$ (Brown and Yoder, 1994). *E. huxleyi* blooms occur in the upper 30 m (see review by Zondervan, 2007), and correlate with a narrow range of sea surface temperatures, light levels, and nutrient depletion (Iglesias-Rodríguez et al., 2002a). Surface stratification appears to be prerequisite (Zondervan, 2007). *E. huxleyi* blooms have also been linked to high ambient $[\text{CO}_3^{2-}]$, though whether this relationship functions as a control on growth is unknown (Merico et al., 2006). Blooms of coccolithophores tend to follow blooms of diatoms, which explains why they correlate with nutrient-depleted conditions, but coccolithophores have shown an ability to grow in nutrient-rich substrate, suggesting limited nutrients alone is not a necessary condition for blooms (Zondervan, 2007). Generally compared with other phytoplankton, *E. huxleyi* have a greater tolerance for high irradiance, an enhanced ability to utilise phosphate and non-nitrate nitrogen, a lesser susceptibility to iron limitation and a greater susceptibility to zinc limitation (Zondervan, 2007).

A recent global survey of coccolithophore populations found large variations in the degree of calcification between species and morphotypes, with more heavily calcified types associated with higher seawater concentrations of carbonate (Beaufort et al., 2011). An exceptional heavily calcified morphotype of *E. hux* was also described by Beaufort et al. (2011) in very low-carbonate concentration seawater, highlighting the complications of assigning global characteristics to a calcifier PFT.

1.2.2 Calcifying Zooplankton

Zooplankton CaCO_3 export is also highly episodic. Planktonic foraminifera generally bloom in spring when deep-dwelling species ascend to feed on blooming phytoplankton stocks, and again in autumn when increased vertical mixing increases food supply (Schiebel, 2002). Their seasonal pattern however is not easily correlated at a global scale to primary production because many forams are omnivorous (Schiebel and Movellan, 2012). Like phytoplankton coccolithophores, most research into heterotrophic calcification has focused on select species (e.g., *Orbulina universa* and *Globigerina bulloides*) for the practical reason that their preservation in sediments is useful for paleoclimate reconstructions (see review by Hood et al., 2006). Estimates of foraminifer biomass production are very poorly constrained, with Schiebel and Movellan (2012) estimating $8.2\text{--}32.7 \text{ Tg C yr}^{-1}$ based on a compilation of published

data. Pteropod dynamics are poorly understood and their CaCO_3 production seems to be even more episodic than foraminifera (summarised in Schiebel, 2002), though a recent data compilation by Bednaršek et al. (2012) suggests pteropod biomass is only episodic in the Southern Hemisphere. Most pteropods appear to live within the 30–60°N latitudinal band, with the lowest populations in Equatorial regions (Bednaršek et al., 2012). Because they secrete aragonite (a more soluble carbonate than calcite) their contribution to global deep export is more difficult to measure (Hood et al., 2006).

1.3 Calcification in Ocean and Climate Models

1.3.1 Fixed Production/Remineralisation Models

The episodic nature of CaCO_3 production is ignored in models that assume globally uniform, fixed CaCO_3 :POC (rain ratio) production and export (e.g., Yamanaka and Tajika, 1996; Dutay et al., 2002; Najjar et al., 2007). Fixed ratio models are tuned to modern ocean carbon profiles and do not resolve biology (upper left green box in Figure 1.3, with sample processes listed in the pink box). They do not contain the requisite mechanistic flexibility needed to model significantly different or transitioning biogeochemical climates. Some attempt to circumvent this limitation by adding parameterisations that adjust CaCO_3 and/or POC export according to changes in a state variable (e.g. depth or pCO_2 , Schneider et al., 2004; Ridgwell et al., 2007a). Chapter 2 illustrates some of the strengths and weaknesses of such a model using the CSIRO-Mk3L (Phipps, 2010) climate model to explore non-linear changes in ocean carbonate saturation state with increasing pCO_2 . As is demonstrated in Chapter 2, one strength of fixed production/remineralisation models is the ease of implementing variable stoichiometry (an onerous task in the more complex UVic ESCM used in subsequent chapters). These types of models are useful for gaining first-order understanding of the interplay between various compartments of the Earth System; e.g., the non-linear impact on ocean interior carbonate saturation state from changes in organic and inorganic carbon pump stoichiometry demonstrated in Chapter 2. A limitation of these types of models is that they cannot simulate feedbacks within Earth System compartments that are internally-derived; e.g., the runaway nutrient transport feedback that arises in the UVic ESCM in Chapter 5.

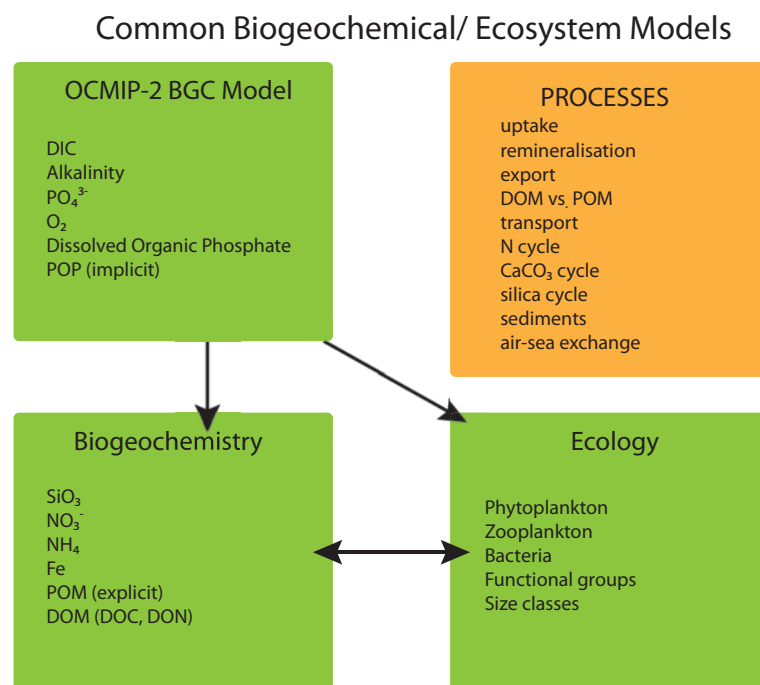


Figure 1.3: Schematic of common ocean biogeochemical model components and hierarchy, modelled after (U.S. Joint Global Ocean Flux Study).

1.3.2 NPZD Models

Other models introduce greater complexity and calculate CaCO_3 export production using a rain ratio and explicit phytoplankton and zooplankton PFTs, while also including carbon and nutrient pools (e.g., Six and Maier-Reimer, 1996; Palmer and Totterdell, 2001; Heinze, 2004; Schmittner et al., 2005; Popova et al., 2006; Hofmann and Schellnhuber, 2009, , bottom two green boxes in Figure 1.3). These models (often abbreviated as NPZD, for nutrients-phytoplankton-zooplankton-detritus) might also include adjustments to CaCO_3 and POC export from changes in state variables or carbonate chemistry (e.g., Six and Maier-Reimer, 1996; Heinze, 2004; Hofmann and Schellnhuber, 2009) but they do not capture shifts in ecosystem structure or physiology and also cannot produce strong PFT seasonality when applied globally. The University of Victoria Earth System Climate Model (UVic ESCM, Weaver et al. 2001, Eby et al. 2009) base version 2.9 fits into this category of model.

1.3.3 Multi-PFT Models

While the simplest single-PFT models can fit data equally well as more complex multi-PFT models when a very limited pelagic regime is considered, increasing the PFTs in a model increases the portability to multiple regimes (Friedrichs et al., 2007). Multiple explicit PFTs can represent non-linear biological responses to resource-based and grazing selective pressures, though within PFTs there will still exist enough variety that results from lab experiments can only provide qualitative descriptions of physiology (Le Quéré et al., 2005). Multi-PFTs have better success in reproducing seasonal succession in regional models (particularly studies focused at high latitudes, e.g., Tyrrell and Taylor, 1996; Gregg et al., 2003; Merico et al., 2004; Litchman et al., 2006) than they have when used globally (e.g., Moore et al., 2002; Aumont et al., 2003; Gregg et al., 2003; Le Quéré et al., 2005) (summarised by Anderson, 2005). The UVic ESCM presented here is a multi-PFT model that includes a mixed phytoplankton type, calcifiers, diazotrophs, and a zooplankton PFT. While model structures varies substantially, a general weakness of this approach is that models are not written with enough flexibility in community structure or biodiversity to allow for emergent PFTs, a key capability for understanding climate change response.

A variety of approaches are taken to representing calcification in multi-PFT models. Implicit calcification of one or more PFTs with fixed rain ratios are common (Le Quéré et al., 2005; Schmittner et al., 2008; Aumont and Bopp, 2006, and the UVic ESCM version described in Chapters 3-5); less common approaches include

co-limitation of calcification by light and temperature (Moore et al., 2002), with a coccolith shedding parameterisation (Tyrrell and Taylor, 1996), or adjustment of the rain ratio with changes in carbonate chemistry (Gehlen et al., 2007; Yool et al., 2013) or latitude (Yool et al., 2011). Other models simply ignore CaCO_3 altogether (Aumont et al., 2003; Gregg et al., 2003; Litchman et al., 2006).

Dissolution of CaCO_3 typically follows the method of Dutay et al. (2002) by assuming that sinking speed and dissolution rates are static (e.g., Le Quéré et al., 2005; Aumont and Bopp, 2006; Schmittner et al., 2005, 2008), but can also be parameterised as dependent on carbonate chemistry (Gehlen et al., 2007). The UVic ESCM version presented in Chapters 3 to 5 includes a prognostic CaCO_3 tracer as well as dissolution rates that are chemistry-dependent.

1.4 Calcification Modelling Applications

The annual fraction of anthropogenic CO_2 emissions remaining in the atmosphere has increased over the past 50 years from 40 to 45% (Le Quéré et al., 2009). The building up of anthropogenic CO_2 in the atmosphere is intensifying greenhouse warming and contributing heat to the oceans. Between 1961 and 2003, the heat content in the upper 700 m increased an average of $16 \pm 3 \times 10^{22}$ J (Domingues et al., 2008), while the heat content in the abyssal 3000 m increased an average of 0.8×10^{22} J per decade between 1985 and 2006 (Kouketsu et al., 2011). Disparate rates of warming between the surface and deep ocean are increasing water column stratification and altering ocean circulation (e.g., Johnson et al., 2008). At the same time, the oceans absorbed an average of 2.2 ± 0.4 Pg C per year between 1990-2000 (Le Quéré et al., 2009). Dissolution of CO_2 in seawater lowers the pH, and the ocean has acidified an average of 0.1 pH units since 1750 (Caldeira and Wickett, 2003). Increasing ocean stratification and sea surface temperature could act as positive feedbacks on the ocean-atmosphere CO_2 equilibrium by furthermore reducing the solubility of CO_2 in seawater (Maier-Reimer et al., 1996; Joos et al., 1999; Chuck et al., 2005).

Future ocean warming and shifting carbon cycle thermodynamics are expected to have global biogeochemical repercussions (recently summarised by Gruber, 2011). Increased water column stratification is expected to increase temperature-dependent biological rates and light availability, as well as to diminish resupply of nutrients to the euphotic zone from the deep ocean (e.g., Bopp et al., 2001; Steinacher et al., 2010), and to reduce gas exchange between the atmosphere, surface and deep ocean (e.g., Sarmiento et al., 1998). Dissolved oxygen concentrations in seawater are de-

clining (e.g., Keeling and Garcia, 2002; Whitney et al., 2007; Stramma et al., 2008) because increasing temperatures and stratification decrease oxygen solubility and transport (e.g., Bopp et al., 2002; Matear and Hirst, 2003), and increase biological oxygen consumption (e.g., Keeling and Garcia, 2002; see Keeling et al., 2010, for a recent review). The net response of ocean biology is highly uncertain and of high concern because biological pathways for carbon export out of the euphotic zone are non-trivial (around 11 Pg C per year, Jin et al. 2006). Climate models incorporating multi-PFT biogeochemistry are tools ideally suited to understanding and quantifying these feedbacks.

1.4.1 Plankton Response to Ocean Warming and Stratification

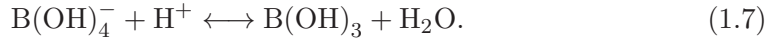
The net marine biological response to ocean warming and stratification in models seems to depend on whether biological processes are considered temperature dependent (Taucher and Oschlies, 2011; Segschneider and Bendtsen, 2013). Coupled ocean-climate models take a varied approach to representing temperature-dependent processes, with most limiting temperature dependency to primary production. These models project decreases in global mean primary production and export over coming decades, caused by stratification reducing nutrient resupply to the euphotic zone (Maier-Reimer et al., 1996; Bopp et al., 2005; Steinacher et al., 2010; Bopp et al., 2013; Moore et al., 2013a). Some models that include temperature-dependent heterotrophy and remineralisation project increases in primary production as a warmer and more stratified euphotic zone enhances nutrient recycling (Schmittner et al., 2005, 2008; Taucher and Oschlies, 2011; Segschneider and Bendtsen, 2013).

In either scenario, alteration of net primary production will also likely be accompanied by changing phytoplankton community composition (Cermeneno et al., 2008; Marinov et al., 2010, 2013). Marinov et al. (2010) find a dual susceptibility in small phytoplankton (a proxy for coccolithophores) versus diatoms, where shifts in the “critical nutrient” threshold over the 21st century are projected to favour diatoms between 45°N and 45°S, and small phytoplankton in the high latitudes. Coccolithophores out-compete diatoms in nutrient poor (deep nutricline) regions, and a shift to coccolithophore rather than diatom-dominated communities could reduce net primary production and provide another positive feedback to atmospheric CO₂ (Cermeneno et al., 2008). A shift to small phytoplankton under warming and stratification would furthermore decrease the export ratio and carbon export rate (Bopp et al., 2005). Should increasing primary production be accompanied by increasing calcification, a positive climate feedback would occur owing to the increasing

release of CO_2 as a by-product of the calcification (Iglesias-Rodríguez et al., 2008; Schmittner et al., 2008). However, changes in timing and strength of coccolithophore seasonal blooms and their associated contributions to CaCO_3 export could be affected by short term, local changes in calcite saturation (Merico et al., 2006), so it remains unclear to what degree coccolithophores might benefit from changes in nutrient and light limitation.

1.4.2 Plankton Response to a Changing CO_2 Thermodynamic Equilibrium

An overview of marine carbonate chemistry is first provided before discussing the role of marine biology. The following chemical reactions govern the marine carbonate system:



These equations represent the dissolution and hydration of carbon dioxide (Equation 1.3), the dissociation of carbon dioxide into bicarbonate, hydrogen and carbonate (Equations 1.4 and 1.5), the self-dissociation of water (Equation 1.6), and the dissociation of borate (Equation 1.7).

Characterisation of the carbonate system requires the estimates of two of the following four measurable quantities: pH, total alkalinity ([TA]), dissolved inorganic carbon ([DIC]), and the CO_2 partial pressure (pCO_2), (Park, 1969; Millero et al., 2006). These quantities are defined as follows:

$$\text{pH} = -\log_{10}([\text{H}^+]) \quad (1.8)$$

$$[\text{TA}] = 2[\text{CO}_3^{2-}] + [\text{HCO}_3^-] + [\text{B(OH)}_4^-] + [\text{OH}^-] - [\text{H}^+] \quad (1.9)$$

$$[\text{DIC}] = [\text{CO}_3^{2-}] + [\text{HCO}_3^-] + [\text{CO}_2(aq)] \quad (1.10)$$

$$\text{pCO}_2 = \frac{1}{K_0^*}[\text{CO}_2(aq)]. \quad (1.11)$$

In Equation 1.11, K_0^* is the inverse of Henry's constant. CaCO_3 precipitation (calcification) removes bicarbonate from solution (Equation 1.1). DIC remaining in the water column is re-partitioned in favour of $\text{CO}_2(aq)$, which raises seawater pCO_2 (Zondervan et al., 2001). The thermodynamic potential of calcification is measured

as calcium carbonate saturation (Ω), where the product of the concentrations of calcium and carbonate are divided by the solubility constant K_{sp} (Equation 1.12).

$$\Omega = \frac{[\text{Ca}^{2+}][\text{CO}_3^{2-}]}{K_{sp}} \quad (1.12)$$

An increase in seawater pCO_2 reduces carbonate concentration (Eqns 1.4 and 1.5) and lowers Ω , reducing the biotic carbonate precipitation rate (Shaojun and Mucci, 1993).

Seventy percent of total calcification is performed by pelagic coccolithophores, foraminifera, and pteropods, making their response to Ω particularly relevant for the global carbon budget (Zondervan et al., 2001). The reduction of CaCO_3 as a response to increased pCO_2 (Riebesell et al., 2000) means less CO_2 is released to the surface mixed layer as a by-product of calcification. This “ CO_2 -calcification feedback” has been examined using simple box (Boudreau et al., 2010) and NPZD models (Heinze, 2004; Ridgwell et al., 2007b) as well as a multi-PFT size class model with calcifying nanoplankton (Gehlen et al., 2007; Gangstø et al., 2011). While only a minor player in global carbon budgets over the short term (Gehlen et al., 2007; Ridgwell et al., 2009; Gangstø et al., 2011) there is an expanding (but still minor) role on a millennial horizon (e.g. Heinze, 2004; Ridgwell et al., 2007b; Gehlen et al., 2007; Boudreau et al., 2010). There are however more immediate changes in nutrient and carbonate profiles that could impact on ecosystem dynamics by decreasing near-surface alkalinity (e.g. Ridgwell et al., 2007b; Boudreau et al., 2010).

Carbon export away from the surface is also impacted by changes in calcification: sinking CaCO_3 might act as ballast for sinking POC (Klaas and Archer, 2002). Ballasting occurs as a result of the waste products of organisms that produce both CaCO_3 and POC, or as the result of physical or biological particle aggregation (Figure 1.4). Biogeochemical models often assume a fixed rain ratio for this ballasting based on global compilation of sediment trap data (see Figure 1.5 from Klaas and Archer, 2002), but increasing pCO_2 can reduce the aggregation of CaCO_3 by coccoliths and affect ballasting rates (Riebesell et al., 2000; Zondervan et al., 2001; Biermann and Engel, 2010).

Enhanced CO_2 in seawater has been observed to increase the rate of POC production by enhancing photosynthesis (Equation 1.2), termed the “POC production feedback” (Zondervan et al., 2001). The efficiency of the biological pump has historically been thought to be controlled not by the availability of CO_2 , which is abundant, but by temperature, light, and the availability of nutrients nitrate (NO_3^-) and phosphate (PO_4^{3-}). Hence the fixed stoichiometry of the photosynthesis equation is

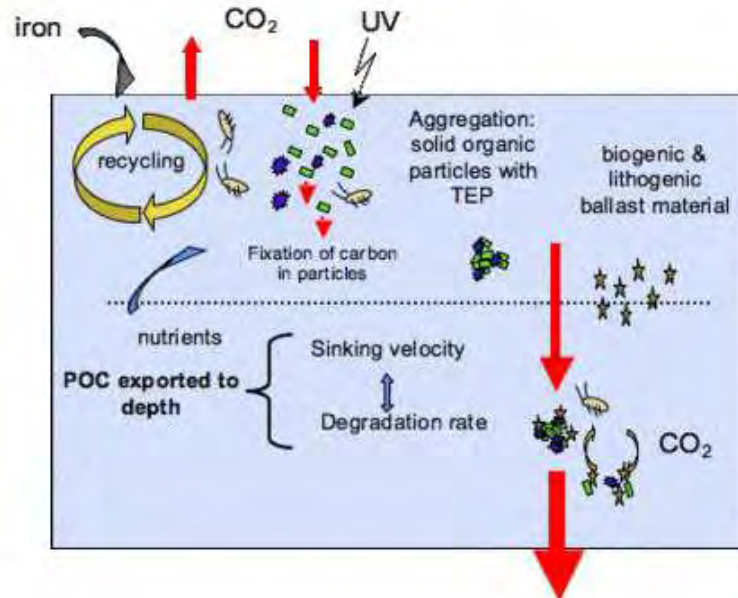


Figure 1.4: Formation of mineral ballast (Alfred Wegener Institute for Polar and Ocean Science).

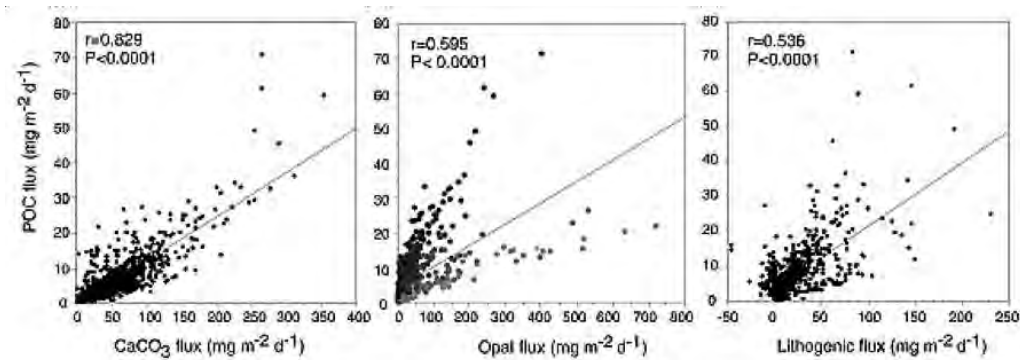


Figure 1.5: Scatterplots, correlation coefficient and probability for individual cup measurements of POC flux versus CaCO₃, opal and lithogenic material fluxes for trap experiments below 1000 m depth. Slopes of the regression lines are 0.126 for CaCO₃, 0.061 for opal and 0.180 for lithogenic material. Shaded circles in the plot of POC versus opal represent the variations in mass opal/total mass ratios levels. The lighter shading corresponds to high mass opal/total mass ratios, dark shading to low mass opal/total mass ratios. Reproduced from Klaas and Archer (2002).

typically applied to marine carbon cycle models, based on the empirically-derived Redfield ratio (Anderson, 1995). Thus enhanced CO₂ model experiments show increasing POC production is accompanied by proportional depletion of nutrient pools, which limits primary production (Bopp et al., 2005).

Mesocosm experiments by Riebesell et al. (2007) suggest carbon-to-phosphate stoichiometry may increase by as much as a factor of 6 under high-pCO₂ conditions, significantly increasing the efficiency of primary producers consuming DIC and reducing the effect of nutrient limitation. Near term (to 2100) high CO₂ model studies that incorporate a variable C:N (or P) ratio (e.g. Schneider et al., 2004; Oschlies et al., 2008; Boudreau et al., 2010) yield only a small additional negative impact on the global anthropogenic carbon budget as coincident changes in ocean physics compensate internally and air/ocean exchange is limited by the solubility pump. On a millennial scale the impact is potentially more significant, though also more theoretical as predicted carbon concentrations far exceed the values for which the Riebesell et al. (2007) linear parameterisation is valid. There are important biogeochemical impacts from enhanced POC production efficiency related to remineralisation, e.g. expanding suboxic zones (Oschlies et al., 2008), a shoaled carbonate compensation horizon and decreasing deep water pH (Boudreau et al., 2010).

A recent meta-analysis of coccolithophore biogeography reveals a clear correlation between high Ω and high coccolithophore calcification, manifesting in regional patterns of differentially calcifying species' relative abundances (Beaufort et al., 2011). Ocean acidification can therefore be expected to selectively modify existing ecological community structures (Ridgwell et al., 2009), though how is largely uncharacterised, particularly in the context of changes in other selective pressures like light, temperature and nutrient availability. Decreasing net calcification (and consequential declining biological CO₂ production) is expected to act as a negative climate feedback (Riebesell et al., 2000; Zondervan et al., 2001; Ridgwell et al., 2007b).

1.4.3 Climate Response to Changes in Ocean Biology- a Thesis Outline

Impacts on global carbon uptake from the above feedbacks are expected to be small relative to the positive climate feedbacks of increasing ocean stratification and seawater temperature (e.g., Maier-Reimer et al., 1996; Joos et al., 1999; Chuck et al., 2005; Ridgwell et al., 2009), and the reduction of solubility caused directly by acidification (Sarmiento et al., 1995).

Looking beyond carbon uptake, changes in open ocean biogeochemistry affected

through ocean warming, acidification and deoxygenation are expected to be major (summarised by Gruber, 2011). The common biogeochemical metrics used to assess these changes are net primary production (NPP), carbon export to the deep ocean, and seawater oxygen content. The common result from modelling studies that systematically explore net biogeochemical changes under anthropogenic forcing scenarios for multiple models is the dependence of outcomes on model parameterisation (e.g., Taucher and Oschlies, 2011; Segschneider and Bendtsen, 2013; Yool et al., 2013; Bopp et al., 2013). Chapter 2 illustrates a non-linear impact on open-ocean Ω owing to combined export production and calcification feedbacks in a simple fixed production and remineralisation ocean model. Changes in biogeochemistry due to changing physics (circulation and temperature) are ignored to isolate the affect of changing stoichiometric ratios on carbon export. The model does not resolve NPP and oxygen content is not examined. Biogeochemistry is approached more holistically in subsequent chapters.

Long-term ocean biogeochemical trends under a high carbon emissions scenario have been speculated to follow those of the 21st century (declining NPP, oxygen content, and carbon export, increasing acidification) (e.g., Moore et al., 2013b). However, Schmittner et al. (2008) demonstrated the combination of reduced stratification and warming-enhanced biological processes after the 21st century result in large increases in global NPP beyond 2100, though oxygen content, carbon export and surface pH still decline. Given the discrepancy between the Schmittner et al. (2008) and other model studies' NPP trend to 2100, it would be interesting to perform a longer-term comparison of coupled models using high emissions scenarios to see if others also show eventual reversal of the NPP trend. So far, no coupled Earth system model studies have been published that examine the ocean biogeochemical response past 2100 using high emissions scenarios and models other than the University of Victoria Earth System Climate Model (UVic ESCM; Weaver et al., 2001; Eby et al., 2009, 2013) that is used by Schmittner et al. (2008). Additionally it is worthwhile to better understand the reason for the discrepancy in the sign of 21st century NPP trends between the Schmittner et al. (2008) study and other model studies. The treatment of temperature sensitivity of biological processes has been shown to influence the sign of the NPP change to 2100 in the UVic ESCM (Taucher and Oschlies, 2011), though other models also include temperature dependent biological processes and still show a decline in NPP over the 21st century (e.g., Yool et al., 2013).

The modified UVic ESCM biogeochemical model presented in Chapter 3 contains four PFTs including an explicit phytoplankton calcifier and a prognostic CaCO_3

tracer. It is a tool uniquely positioned among Earth Models of Intermediate Complexity (EMICs) because it is of a coarse enough resolution to run long simulations, yet it has the mechanistic realism to fully explore feedbacks in the ocean carbon cycle. Chapter 4 details the application of a theoretical acidification handicap on the calcifier population in the UVic ESCM, and describes the effect on phytoplankton biogeography in the model. This handicap acts to reduce calcification and ballasting even while NPP increases. Chapter 5 describes the different responses of the UVic ESCM to transient greenhouse gas forcing with and without calcifiers, and with and without prognostic CaCO_3 over long simulations extending to year 2400. Firstly, the discrepancy in 21st century NPP trend between the UVic ESCM and other EMICs is attributed to the grazing parameterisation. The latest UVic ESCM control version is demonstrated to now agree with similar EMICs over the 21st century with respect to the common biogeochemical metrics. Then two dominating ocean feedbacks are described; the first one occurs under smaller changes in ocean temperature and is controlled by physical processes, in which the choice to include or exclude the calcifier PFT controls the sign of the NPP response to warming. Transition to the second dominating ocean feedback occurs at higher temperature changes in all models, though when is determined by phytoplankton community composition. This second feedback is controlled by accelerated nutrient recycling by microbes in all models, though is shown to be sensitive to whether a prognostic ballast model is included.

Chapter 2

The Combined Impact of CO₂-Dependent Parameterisations of Elemental and Rain Ratios on Ocean Carbonate Saturation

A version of this chapter appeared online in Biogeosciences Discussions (Kvale et al., 2011). Contributions by the co-authors listed on the manuscript were largely editorial. Copyright is retained by the authors.

Future changes to the organic carbon and carbonate pumps are likely to affect ocean ecosystem dynamics and biogeochemical cycles. In this chapter, biological dependencies of rain and elemental ratios on pCO₂ are implemented in a coupled Biogeochemistry-Ocean Model, the CSIRO-Mk3L, to establish extreme-case carbonate saturation vulnerability to enhanced POC export and decreased CaCO₃ export at year 2500 using IPCC Representative Concentration Pathway 8.5. Surface carbonate saturation is relatively insensitive to the combined effects of variable ratios (an anomaly of less than 10% of the corresponding change in the control configuration by year 2500), but the global zonally-averaged ocean interior anomaly due to these feedbacks is up to 130% by 2500. A combined interaction between organic and carbonate pumps is found in export production, where higher rates of photosynthesis enhance calcification by raising surface alkalinity. This combined effect has a negligible influence on surface carbonate saturation but does significantly in-

fluence ocean interior carbonate saturation fields (an anomaly of up to 45% in 2500) owing to different CaCO₃ and POC remineralisation length scales. The strongest sensitivity to the feedbacks occurs in low-latitude remineralisation zones below regions of enhanced biological production, where dissolved inorganic carbon rapidly accumulates.

2.1 Model and Experimental Design

The coupled climate-carbon model, CSIRO-Mk3L (Phipps, 2010), is employed in ocean-only mode, as the focus of the study is ocean biogeochemistry. The Mk3L ocean has a resolution of 2.8 degrees longitude by 1.6 degrees latitude with 21 vertical levels, with a similar structure to the higher-resolution CSIRO Mk3 and CSIRO Mk2 models (Gordon et al., 2002; Hirst et al., 1996). The background mean ocean circulation simulation has been described previously by Najjar et al. (2007); Dutay et al. (2002). The ocean biogeochemistry component of Mk3L follows Matear and Hirst (2003), using OCMIP protocol (Dutay et al., 2002) for CO₂ air/sea gas exchange and carbonate chemistry.

2.1.1 Elemental Ratio Parameterisation

In order to explore the interaction between biological carbon pump feedbacks, dependencies on pCO₂ are added to the fixed Redfield carbon-to-phosphate (POC:POP, referred to hereafter as an ‘elemental ratio’) and carbonate-to-phosphate (CaCO₃:POP, the rain ratio) parameterisations. POC export (F^{POC}) and POP export (F^{POP}) are varied with a linear response scaled against pre-industrial seawater pCO₂ (Riebesell et al., 2007, and Figure 2.1):

$$F^{\text{POC}} = 106F^{\text{POP}}F_{\text{scale}} \quad (2.1)$$

$$F_{\text{scale}} = 1 + \frac{2}{700} \frac{16}{106} (\text{pCO}_2 - 280). \quad (2.2)$$

Tagliabue et al. (2011) recently explored the sensitivity of carbon export to assumptions surrounding stoichiometric enhancement of remineralisation and found that the assumption used herein (equal enhancement of production and remineralisation) constitutes a high-end approximation of carbon export response, whereas a shedding of extra carbon as DOC in the surface reduces the POC export at 100 m depth.

The elemental ratio parameterisation explores response to ocean acidification only. Stoichiometric ratios might also be increased by increasing ambient temperature (Woods et al., 2003) or decreased mixed layer depth (Diehl et al., 2005).

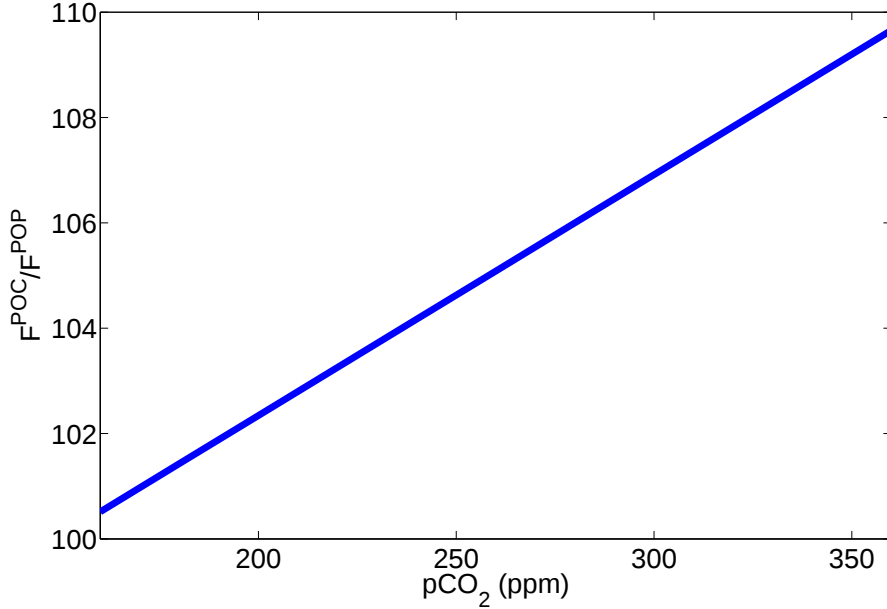


Figure 2.1: Linear scaling of $F^{\text{POC}} : F^{\text{POP}}$ by pCO_2 .

2.1.2 Rain Ratio Parameterisation

Biological calcification in the model contains an additional scaling factor from Ridgwell et al. (2007b) to vary carbonate production (γ) with local calcite saturation, where η is a power parameter (with a value of 0.81) controlling the non-linearity of the calcification response.

$$\gamma = (\Omega - 1)^\eta \quad \text{For } \Omega > 1.0 \quad (2.3)$$

$$\gamma = 0.0 \quad \text{For } \Omega \leq 1.0 \quad (2.4)$$

Carbonate export (F^{CaCO_3}) is linked to POP export by a calculated rain ratio modified by γ :

$$F^{\text{CaCO}_3} = \gamma \times r_0^{\text{CaCO}_3:\text{POP}} \times F^{\text{POP}} \times r_0^{\text{POC:POP}} \quad (2.5)$$

where $r_0^{\text{CaCO}_3:\text{POP}}$ is a globally fixed ratio (Ridgwell et al., 2007b) and $r_0^{\text{POC:POP}}$ is fixed following Equation 2.1 without the scaling factor F_{scale} . Figure 2.2 illustrates the scaling. Note that carbonate export is used as a proxy for calcite production—other parameterisations exist; Ridgwell et al. (2009) and Gangstø et al. (2011) provide two recent reviews. The Ridgwell et al. (2007b) parameterisation is one of the

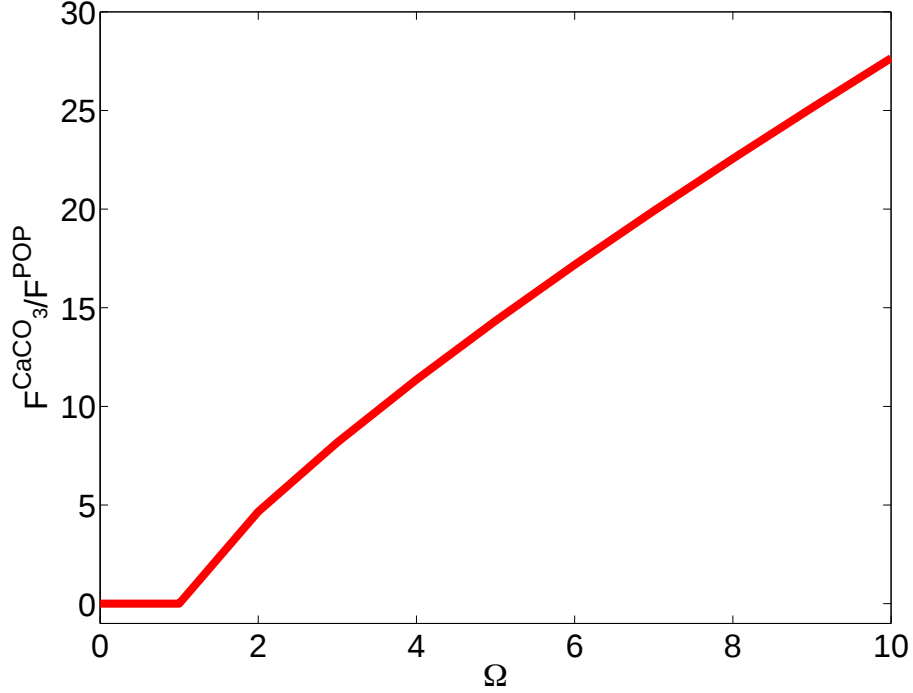


Figure 2.2: Scaling of $F^{\text{CaCO}_3} : F^{\text{POP}}$ by Ω .

more sensitive parameterisations (Ridgwell et al., 2009), and is therefore applied to this study for examining high-end vulnerability. This rain ratio parameterisation does not account for particle aggregation (which would allow variable sinking rates), nor does it differentiate between particle classes, but it does demonstrate a latitudinal dependency which roughly aligns with observations, owing to the calcite saturation scaling factor γ .

Following OCMIP protocol (Dutay et al., 2002), model CaCO₃ dissolution below the surface layer utilises a rigid exponential depth dependency so changes to surface CaCO₃ production mostly affect the depth of complete CaCO₃ dissolution; i.e. increasing CaCO₃ production yields a more penetrating CaCO₃ inorganic chemical signal in the water column. The current arrangement maintains independence between inorganic and organic carbon pump feedbacks while allowing for interactions with carbonate chemistry from both. Note this independence is only true below the surface; the scaling factors applied at the surface for CaCO₃ and POC with respect to POP (Eqns. 2.1 and 2.5) allow for direct interaction between organic and inorganic export feedbacks via alteration of surface pCO₂ and calcite saturation.

2.1.3 Experimental Design

Four different configurations of the model (CONTROL, RAIN, REDFIELD, RAIN-RED) are spun up for six thousand years under a constant atmospheric concentration of 278 ppm to reach pre-industrial equilibrium, and are then forced by an atmospheric carbon concentration pathway following RCP8.5 (Riahi et al., 2007) to 2500. This scenario exhibits growth in atmospheric CO₂ concentrations to 936 ppm by 2100 and 1962 ppm by 2250, whereupon the concentration remains constant until 2500. The CONTROL configuration utilises globally uniform fixed Redfield (Equation 1.2) and rain ratios (CaCO₃:POP value of 8.48). The RAIN configuration parameterises the rain ratio following Ridgwell et al. (2007b, Eqns. 1.1 to 1.12 and 2.3 to 2.5), where $r_0^{\text{CaCO}_3:\text{POC}}$ is set to 0.02 (the negative one standard deviate given in Ridgwell et al. (2007b)) and the rain ratio is solved prognostically. The REDFIELD configuration fixes the rain ratio using the CONTROL value but varies elemental stoichiometry according to Eqns. 2.1 and 2.2. A 2 ppm discrepancy exists between the F_{scale} equilibrium and the RCP 8.5 pre-industrial atmospheric concentration, but the effect is negligible. Finally, RAINRED varies both rain and elemental ratios. Note only CaCO₃ and POC vary between runs; POP does not change across configurations. Also, as this is an ocean-only model, increasing CO₂ concentrations in the experiments impact neither the global radiative balance nor ocean circulation, so no physical feedback to atmospheric CO₂ is simulated.

2.1.4 Model Evaluation

The physical ocean module of Mk3L is fully evaluated in Phipps (2010). Integrated global inorganic carbon fields vary less than 0.4% within model configurations in equilibrium. Figure 2.3 compares global zonally averaged RAIN and REDFIELD pre-industrial equilibrium DIC, alkalinity, calcite saturation, and nitrate with GLODAP gridded observations (Key et al., 2004). Varying the rain ratio with respect to pCO₂ increases the alkalinity and DIC of the surface and intermediate water and slightly lowers the abyssal carbonate saturation values. Differences in carbonate saturation within the deep ocean across configurations are within tenths of a point. Nitrate is slightly overestimated in the abyssal ocean, because of the model's overturning strength which is somewhat weaker than present day estimates (Phipps, 2010).

Figure 2.4 compares GLODAP and model full fields for the surface ocean. The RAIN and RAINRED models better simulate high GLODAP alkalinity values in the surface gyres than the CONTROL and REDFIELD models. All models show

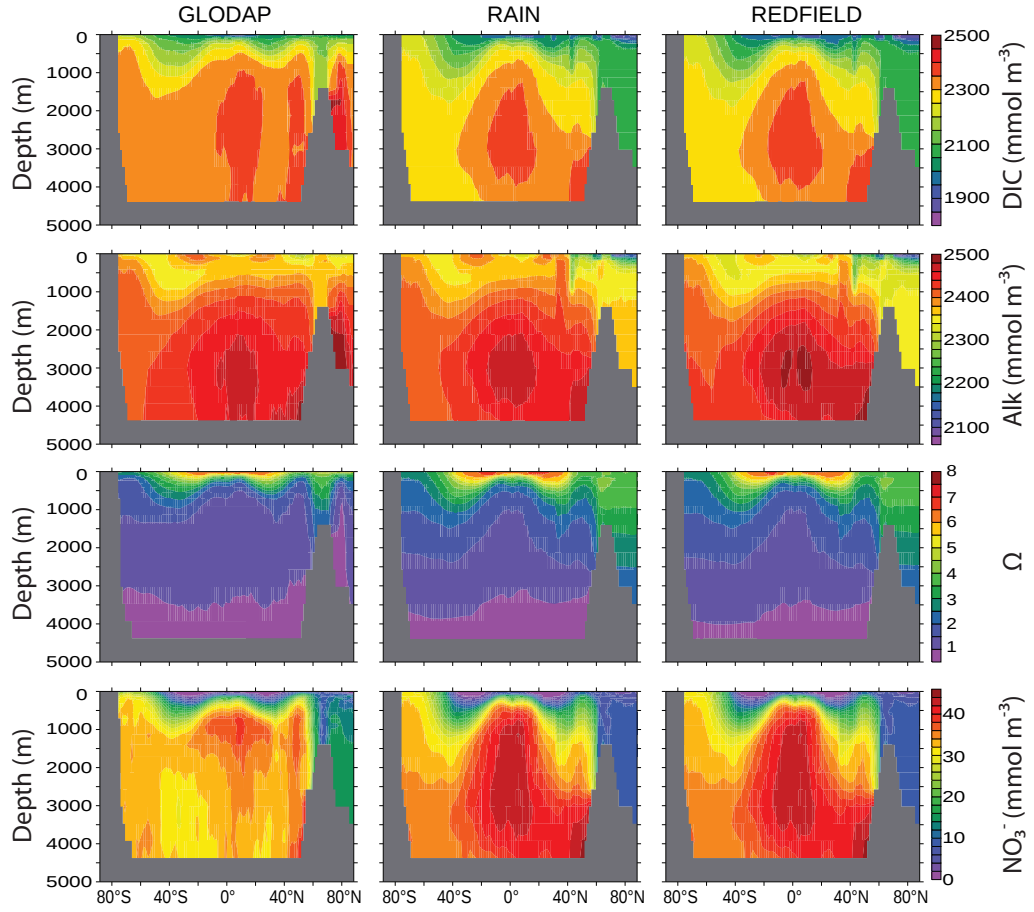


Figure 2.3: Global zonally averaged GLODAP observations (left column) and pre-industrial Mk3L simulation results (RAIN- middle column, and REDFIELD- right column) in mmol m⁻³. Top row is DIC, second row is alkalinity, third row is calcite saturation (unitless), bottom row is nitrate. The apparent plot artefact at 40°N is due to values simulated in the Mediterranean.

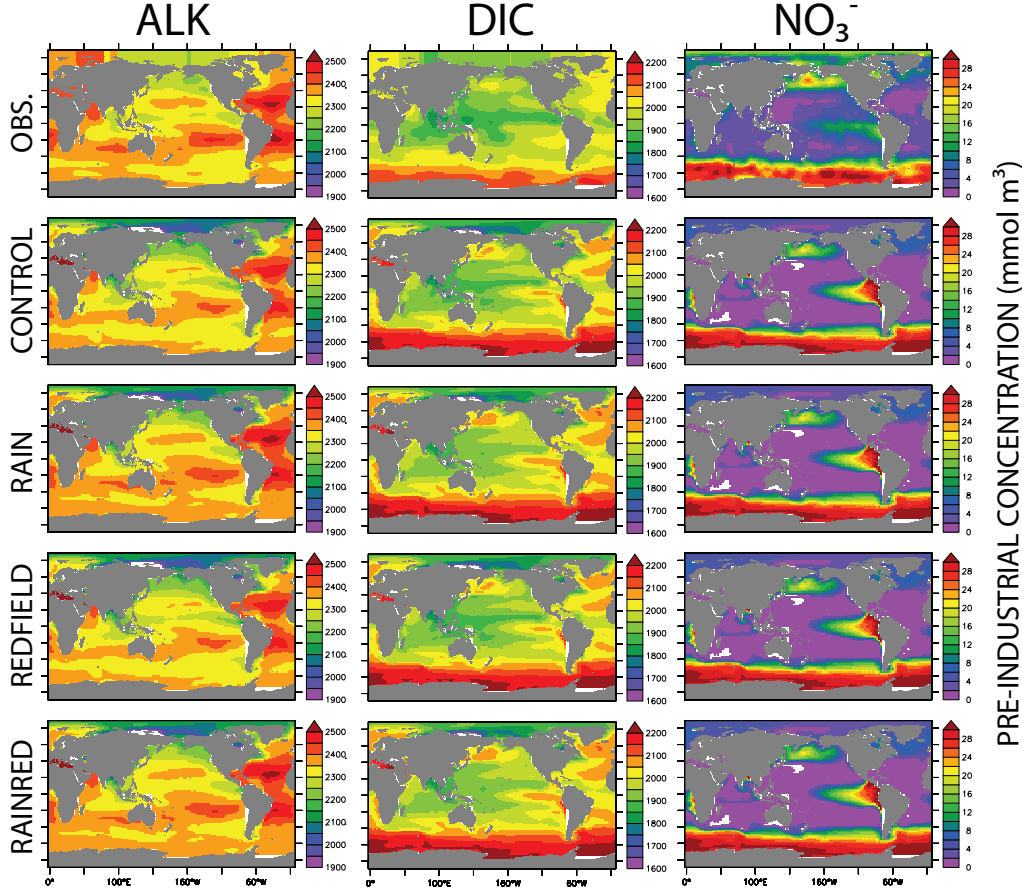


Figure 2.4: Surface GLODAP observations (top row) and pre-industrial Mk3L simulation results (CONTROL- second row, RAIN- third row, REDFIELD- fourth row, RAINRED, bottom row) in mmol m^{-3} . Left column is alkalinity, middle column is DIC, right column is nitrate.

a bias towards high surface DIC and nitrate values, particularly in the equatorial upwelling zones.

Generally good agreement of model equilibrium carbon distributions with gridded observations suggests that POC and CaCO_3 export estimates from the model surface (a depth layer extending the upper 25 m) are appropriate, despite the apparently large initial export value for POC (about 20 Pg C per year for all model configurations) shown in Figure 2.5 at year 1900. Model POC export at 80 m (level 3 in Mk3L) is roughly half of the export at 25 m, which is in agreement with the Jin et al. (2006) estimate of 9.8 Pg C per year at 75 m depth. Model CaCO_3 export is more conservative than POC because of its longer remineralisation length scale.

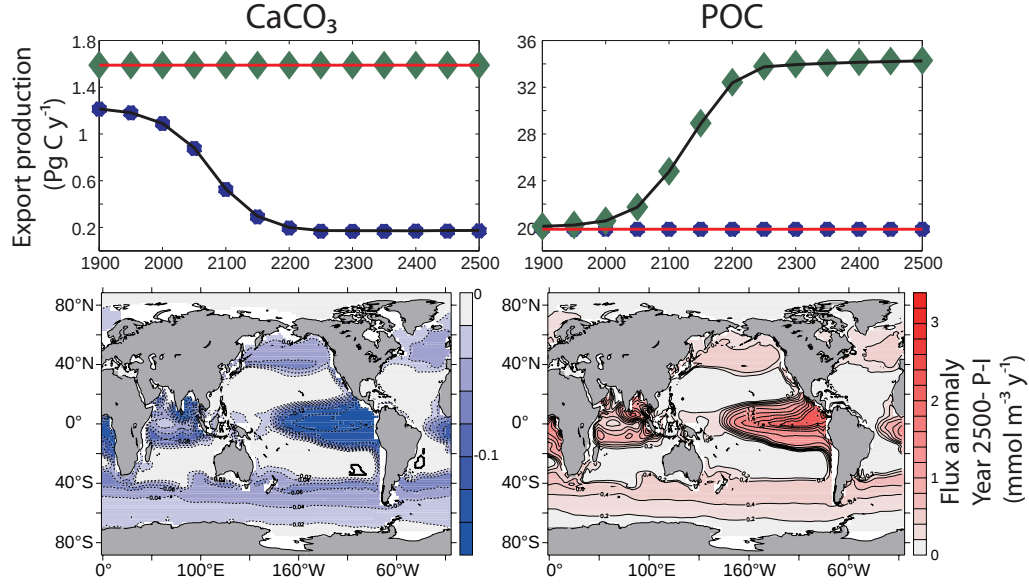


Figure 2.5: Timeseries of integrated global CaCO₃ (top left plot) and POC (top right plot) surface export production in Pg C per year. Color key is as follows: CONTROL (red), RAIN (blue), REDFIELD (green), RAINRED (black). Bottom plots show the change in CaCO₃ (left plot) and POC (right plot) fluxes at year 2500 relative to the pre-industrial equilibrium in the RAIN and REDFIELD configurations, respectively. Units in the bottom plots are mmol m⁻³ y⁻¹.

CaCO₃ flux at 25 m is 1.2 to 1.6 Pg C per year (compare with the Jin et al. 2006 estimate of 1.14 Pg C per year at 75 m depth).

2.2 Transient Simulations

2.2.1 CaCO₃ and POC Surface Export

Rain and elemental ratio feedbacks alter CaCO₃ and POC export from the surface layer. Figure 2.5 summarises globally integrated annual surface carbon export from year 1900 to year 2500 for each configuration and also shows the change in surface CaCO₃ and POC export fluxes from pre-industrial equilibrium to year 2500 for the RAIN and REDFIELD configurations, respectively. CaCO₃ and POC export remain constant over the CONTROL simulation (red lines) because both rain and elemental ratio feedbacks are fixed constants. RAIN (blue stars) CaCO₃ export decreases relative to CONTROL because as surface calcite saturation decreases with

increasing pCO₂, less calcification occurs in the surface layer and less CaCO₃ is exported. RAIN CaCO₃ also has a lower initial value from CONTROL owing to this export dependence on surface calcite saturation. POC export is unaffected by changes to the rain ratio and hence RAIN POC mirrors CONTROL POC. CaCO₃ export in the REDFIELD experiment (green diamonds) is unaffected by changes in elemental stoichiometry and hence REDFIELD CaCO₃ mirrors CONTROL CaCO₃. The POC field in RAINRED (black lines) mirrors that of REDFIELD POC, which like REDFIELD sees increases in POC export as pCO₂ increases the efficiency of the organic carbon pump. Initial POC values for REDFIELD and RAINRED are slightly higher than those of RAIN and CONTROL owing to the dependence of export on pCO₂ anomaly from 278 ppm, which has increased by year 1900. Note that RAINRED CaCO₃ does not exactly mirror RAIN CaCO₃, even though in the REDFIELD configuration CaCO₃ export is shown to be unaffected. This incongruence is nearly indistinguishable in Figure 2.5 but crucially reveals a “combined” exchange between rain and elemental ratio feedbacks in the RAINRED simulation, where reduced CaCO₃ export (calcification) due to the decreasing carbonate saturation in the inorganic carbon pump is slightly tempered by the additional release of carbonate owing to an enhanced organic carbon pump. Said another way, the calculated direct response in abyssal carbonate saturation owing to changes in the rain ratio, when summed with the calculated direct response owing to changes in elemental ratios, does not equal the actual model response in abyssal carbonate saturation. This combined chemical exchange is summarised in Figure 2.6 and revolves about the enhanced consumption of free hydrogen in Equation 1.2 as part of enhanced POC formation. Figure 2.6 is similar to a Bond graph (common in electrical engineering), where individual components (photosynthesis, dissolution, etc.) are connected through effort (H⁺, CO₃²⁻, etc.) and flow (positive and negative gains). In the figure, there are 3 routes that lead from increased surface CO₂ to a change in deep ocean Ω. Route 1 follows the green line through the organic carbon pump. Route 2 follows the orange line through the carbonate pump. Route 3 follows the blue line between the organic carbon and carbonate pumps. The blue and red gain lines which connect the components and effort show non-quantitative gains resulting from an increase in component A, which causes component B to either decrease (negative gain) or increase (positive gain). Route 3, the combined impact via both carbon and carbonate pumps, occurs because inorganic carbon chemistry dictates a reduction in free hydrogen resulting in an addition of carbonate ions, according to $\text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-}$. This small increase in carbonate ion buffers the carbonate saturation which controls CaCO₃ export production in the model (shown as a blue

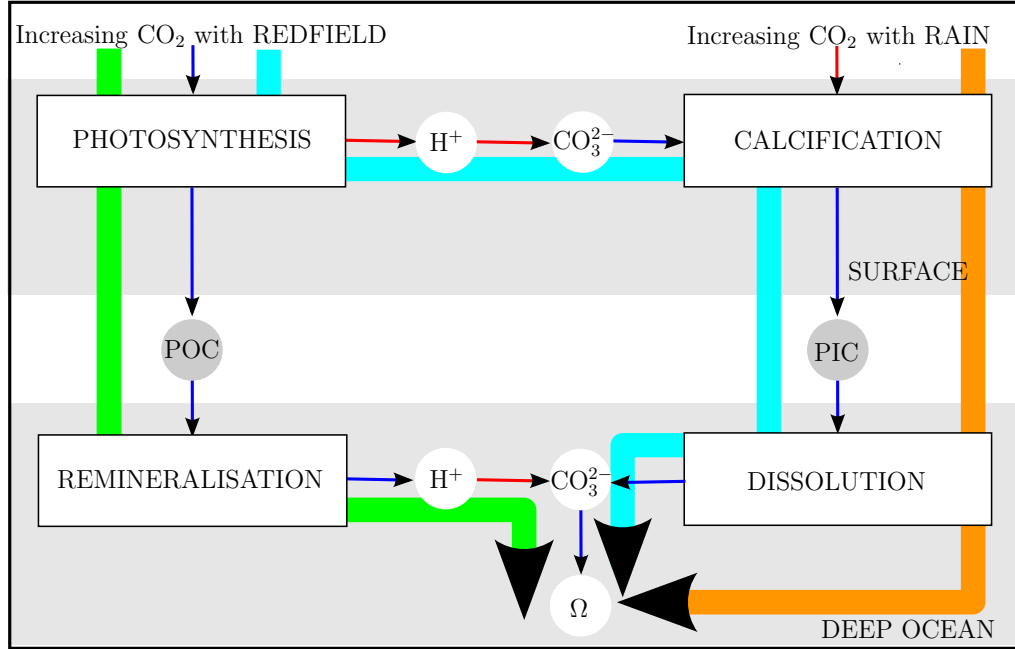


Figure 2.6: A qualitative schematic of feedback processes operating between organic and inorganic carbon pumps and carbonate saturation. The impact of the variable rain and elemental ratio parameterisations on deep ocean carbonate saturation are shown as coloured pathways with fat arrows: rain (orange), elemental (green), rain and elemental (blue). Positive gains (an increase in A leads to an increase in B) are presented in thin blue and negative gains (an increase in A leads to a decrease in B) in thin red. An even number of negative gains (red arrows) in a pathway sum to a positive feedback, while an odd number of negative gains remain negative. The sign of the net feedbacks do not sum across pathways.

pathway). In the RAINRED configuration, CaCO₃ formation is still reduced by the decreased saturation, but not as much as it is in the RAIN configuration (orange pathway) where no additional carbonate input from altered photosynthesis occurs. Therefore, an even number of negative gains in Route 3 creates a net positive feedback (an increase in CO₂ leads to an increase in Ω), while an odd number of gains in Routes 1 and 2 creates a net negative feedback (an increase in CO₂ leads to a decrease in Ω). Figure 2.6 says nothing about the cumulative effects of combining the net feedbacks in the 3 routes, nor does it say anything about the relative strengths of the net feedbacks.

2.2.2 Carbonate Saturation

The impact of variable CaCO₃ and POC export production on ocean carbonate saturation in the RAINRED configuration can be quantified using snapshot and anomaly plots, shown in Figure 2.7. By 2500 only a shallow region between 40 degrees North and South latitude meets the CaCO₃ production criteria (Equation 2.3). In the third row, RCP 8.5 forcing over the simulation is removed by subtracting the pre-industrial equilibrium state from 2500, and then subtracting that difference for the CONTROL run from the remainder (e.g., $\Delta\text{RAINRED}-\Delta\text{CONTROL}$ where Δ is year of simulation minus pre-industrial state). As mentioned in Section 2.2.1, the added effect of RAIN and REDFIELD is not equal to the combined effect in the RAINRED simulation. The combined component of these anomalies are shown in the bottom row. Positive combined anomaly values indicate a mitigation response for carbonate saturation. Negative combined anomaly values indicate an amplification of the carbonate saturation anomaly.

A striking pattern emerges in the additional total and combined effects of the feedbacks (Figure 2.7). By 2500 the global zonally averaged RAINRED anomaly is up to 0.25 units larger than that of CONTROL in the tropical abyssal ocean (third row, leftmost panel), an anomaly more than twice as large as the change in $\Delta\text{CONTROL}$ over this time (not shown). The RAINRED anomaly contributes up to 45% of the global zonally averaged background RAINRED carbonate saturation in this same region, even though the additional impact on carbonate saturation at the surface is less than 10% (seen when comparing leftmost panels in the second and third rows). This increasing impact on carbonate saturation in the ocean interior away from the surface is due to the decoupling of CaCO₃ and POC remineralisation owing to differing remineralisation length scales, where POC remineralisation is accelerated by the variable elemental ratio but CaCO₃ dissolution varies in depth of complete dissolution only.

A positive (mitigative) combined response is present in the ocean interior (bottom left panel), and is valued at roughly 10% of the global zonally averaged RAINRED anomaly (seen when comparing leftmost panels in the third and fourth rows). A weak negative combined response is found in the upper 500 m (up to 1.5% of $\Delta\text{CONTROL}$, not shown). This RAINRED amplification at the surface and mitigation at depth is due to the combined effect of POC enhancement on CaCO₃ production described earlier and shown in Figure 2.6. Reduction of CaCO₃ export production in RAINRED is tempered by the additional availability of carbonate owing to enhanced POC production, which allows for slightly reduced carbonate saturation at the surface and

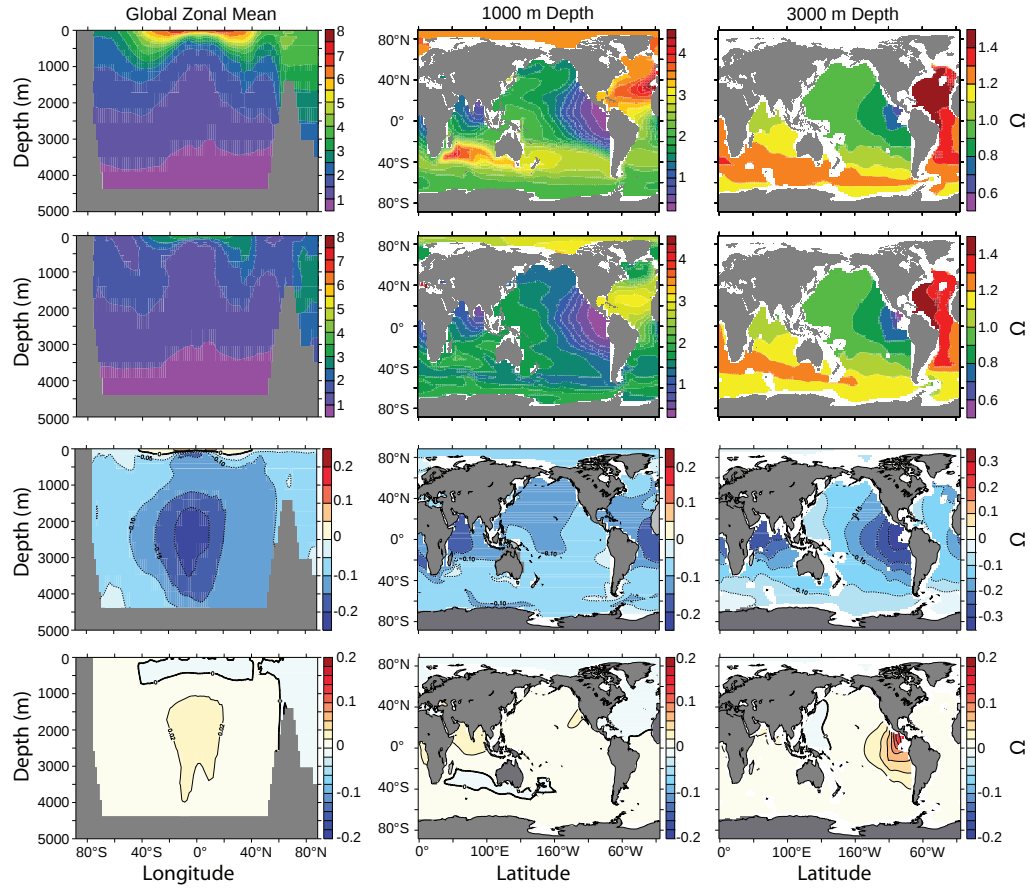


Figure 2.7: Pre-industrial (first row) and year 2500 (second row) RAINRED calcite saturation, and year 2500 RAINRED calcite saturation ($\Delta\text{RAINRED} - \Delta\text{CONTROL}$, third row) and combined ($\Delta\text{RAINRED} - [\Delta\text{RAIN} + \Delta\text{REDFIELD}]$, fourth row) anomalies. Left column shows the global zonal mean. Middle column is a map view at 1000 m depth. Right column is a map view at 3000 m depth.

enhanced saturation at depth, relative to what would be seen in purely independent carbon and inorganic carbon pump feedbacks.

Tropical regions show greater variability in Ω than what the global mean profile plots in Figure 2.7 suggest. Figure 2.7 middle and right columns show the strongest impacts on carbonate saturation are confined to regions with strong POC enhancement, such as upwelling zones in eastern ocean basins. RAINRED anomalies in these regions are the largest nearing depths of complete CaCO₃ dissolution, hence are more apparent in the 3000 m depth plots (right column) than the 1000 m plots (middle column). The eastern Pacific in particular shows the strongest response, where the Δ RAINRED anomaly is over 0.3 units at 3000 m depth (third row, right panel), a saturation change eight times that of Δ CONTROL in this same region (not shown). The combined anomaly (bottom right panel) in this region is also significant, with a mitigating effect of about 20% the RAINRED anomaly value in this region (seen when comparing rightmost panels in the third and fourth row). As POC production is most enhanced in this region, the impact on CaCO₃ export production extends the deepest within this region by the fixed CaCO₃ dissolution gradient. In contrast to the eastern Pacific, the Indian Ocean has generally less POC and CaCO₃ production and hence has a weaker combined signal. While enhanced carbonate undersaturation and a small combined positive anomaly are seen by year 2500 in the Indian Ocean, the signal does not extend as deep as in the Pacific and the maximum combined anomaly values peak around 1000 m depth (bottom middle panel).

2.3 Summary and Conclusions

This study has demonstrated the sensitivity of the interior ocean carbonate saturation to the combined effects of varying elemental and rain ratios. CO₂-induced calcification and POC production feedbacks operate in the same region of the ocean interior and may both mitigate and enhance each other. As such, caution is warranted when assessing ocean carbonate chemistry using only one feedback at a time. This is particularly true in the low-latitude sub-surface and abyssal ocean regions, which show particular sensitivity to the combined contribution of the dual feedbacks of varying elemental and rain ratios. As carbonate saturation is a commonly accepted proxy for calcification, such a sensitivity has relevance for predicting changes in ecosystem dynamics in an increasingly acidic marine environment. These results build upon previous work, most notably Boudreau et al. (2010), who calculated a strong added rain and elemental ratio feedback on ocean interior pH and carbonate

compensation depth in a box model. These results also show that biogeochemical feedbacks have the potential to significantly alter carbonate saturation without coincident changes in the mean circulation, and may explain at least part of a mechanism operating around high carbon perturbation events in the past (434, 350, 250, and 200 M.A.) when calcification shows evidence of both lasting and preferential depression with respect to other forms of production (as reviewed by Veron, 2008), even in the absence of a stagnant circulation (e.g. Winguth and Maier-Reimer, 2005). It must, however, be stressed that this study is a sensitivity study of biogeochemical parameterisations. Results are not projections of future ocean chemical climate because the model includes neither sediments nor radiative feedback. Likewise, the parameterisations reflect observed responses of an incomplete sampling of the biodiversity found in the global ocean, include neither multiple functional types nor multiple trophic levels, and the REDFIELD parameterisation in particular is tested beyond its calibration limit of 1050 ppm. Additional experimental limitations might include nutrient trapping as a side-effect of model resolution (e.g. Aumont et al., 1999), which would contribute to an overestimate of the magnitude of the combined effect, though this is likely a small influence as only anomalies are discussed and circulation remains unchanged in the experiments. The dependence of CaCO₃ dissolution on depth and not Ω might, on the other hand, be contributing to an underestimate of the combined effect by artificially lowering the depth of CaCO₃ dissolution below the zone of POC remineralisation. While the physical justification of widespread Ω -dependent CaCO₃ export is debatable (as summarised by Sarmiento and Gruber, 2006, pages 371-374), severely undersaturated water such as what is calculated in this hypothetical parameter test does approach a calcite dissolution e-folding timescale of a similar order to that of carbonate particle sinking. Should subsurface pooling of DIC owing to enhanced POC export and remineralisation accelerate CaCO₃ dissolution, the combined carbonate anomaly would be enhanced following the deep ocean schematic in Figure 2.6.

The potentially critical omissions of sediment, radiative forcing and carbonate chemistry-dependent CaCO₃ dissolution feedbacks, in addition to the simple structure of the biological parameterisation, limits the usefulness of the CSIRO-Mk3L for testing earth system biogeochemical responses to environmental change. Subsequent chapters present a model, the UVic ESCM, that includes sediments, radiative forcing, and chemistry-dependent dissolution, as well as a more complex biological structure.

Chapter 3

A New Calcification Submodel for the UVic ESCM

A version of this chapter is currently under review online in Atmosphere-Oceans (Kvale et al., 2014). Contributions by the co-authors listed on the manuscript include both technical assistance as well as editorial comments. Copyright is retained by the journal pending formal acceptance.

Marine calcifiers as a plankton functional type (PFT) are a crucial part of the global carbon cycle, being responsible for much of the carbon export to the deep ocean entering via biological pathways. Deep ocean carbon export through calcifiers is controlled by physiological, ecological and biogeochemical factors. This chapter describes the implementation of a calcifying phytoplankton PFT in the University of Victoria Earth System Climate Model (UVic ESCM), and mechanistic improvements to the representation of model carbon export (a full calcite tracer, carbonate chemistry dependent calcite dissolution rates, and a ballasting scheme). The UVic ESCM now fills a niche in Earth System modelling that was previously unoccupied in that it is relatively inexpensive to run (up to 750 years in 1 day using Intel Xeon E5 processors), yet resolves the complete Earth System carbon cycle including prognostic calcium carbonate and a separate calcifier PFT. The model is now ideally suited to test the parameter space of feedbacks between the carbonate and carbon cycles and the climate system as transient simulations. The described modifications improve the mechanistic realism of the UVic ESCM carbon cycle without negatively impacting performance with respect to observed carbon and nutrient fluxes. Primary production, export production, particulate organic carbon and calcite fluxes all fall within independently observed estimates.

3.1 Model Description

The UVic Earth System Climate Model (UVic ESCM, Weaver et al. 2001, Eby et al. 2009) version 2.9 is a coarse-resolution ($1.8^\circ \times 3.6^\circ \times 19$ ocean depth layers) ocean-atmosphere-biosphere-cryosphere-geosphere model. It has a history of applications ranging from climate connections with land surface dynamics (Matthews et al., 2003, 2005; Meissner et al., 2003), to sea ice dynamics (Mysak et al., 2005; Sedlacek and Mysak, 2009), ocean circulation (Spence and Weaver, 2006), Earth System thresholds, tipping points, and nonlinearities (Fyke and Weaver, 2006; Nof et al., 2007; Weaver et al., 2007; Meissner et al., 2008; Zickfeld et al., 2011), paleoclimate (Meissner, 2007), and ocean carbon cycle feedbacks (Schmittner et al., 2008; Oschlies et al., 2008; Meissner et al., 2012). The role of the global carbon cycle in these various applications has been a key research interest.

Schmittner et al. (2005, 2008) added an ocean carbon cycle submodel to the UVic ESCM with two phytoplankton PFTs (general phytoplankton and diazotrophs) and one zooplankton PFT, as well as particulate detritus. The PFTs and detritus are linked to biogeochemical tracers oxygen, nitrate and phosphate through fixed Redfield stoichiometry using a base unit of $\text{mmol nitrogen m}^{-3}$. PFT contributions to the inorganic carbon cycle (alkalinity and DIC tracers) are calculated from POC production and remineralisation using a fixed rain ratio. Ecological interactions within the Schmittner et al. (2005, 2008) model were improved by Keller et al. (2012). The primary differences between the Schmittner et al. (2005, 2008) and Keller et al. (2012) versions are the application of a mask to account for phytoplankton iron limitation, a new formulation of grazing by zooplankton, and changed growth rate parameter values for phytoplankton and zooplankton.

In this latest version the general phytoplankton PFT is exactly replicated, but given new parameter values to reflect key physiological characteristics of calcifiers, albeit biased towards *E. huxleyi*. This new model version therefore contains “calcifiers”, “diazotrophs” and “general phytoplankton”. The general phytoplankton PFT includes diatoms as well as all other autotrophic non-calcifying phytoplankton. Just as the general phytoplankton PFT cannot perfectly describe the physiology or ecology of any of the individual classifications of phytoplankton it represents, the calcifying PFT represents a group of phytoplankton with a common role in the carbonate cycle (calcification) and a few generalised shared physiological traits. CaCO_3 is calculated prognostically as a model tracer and dissolution of calcifier and zooplankton export is now dependent on ambient carbonate concentration. The new model schematic is shown in Figure 3.1.

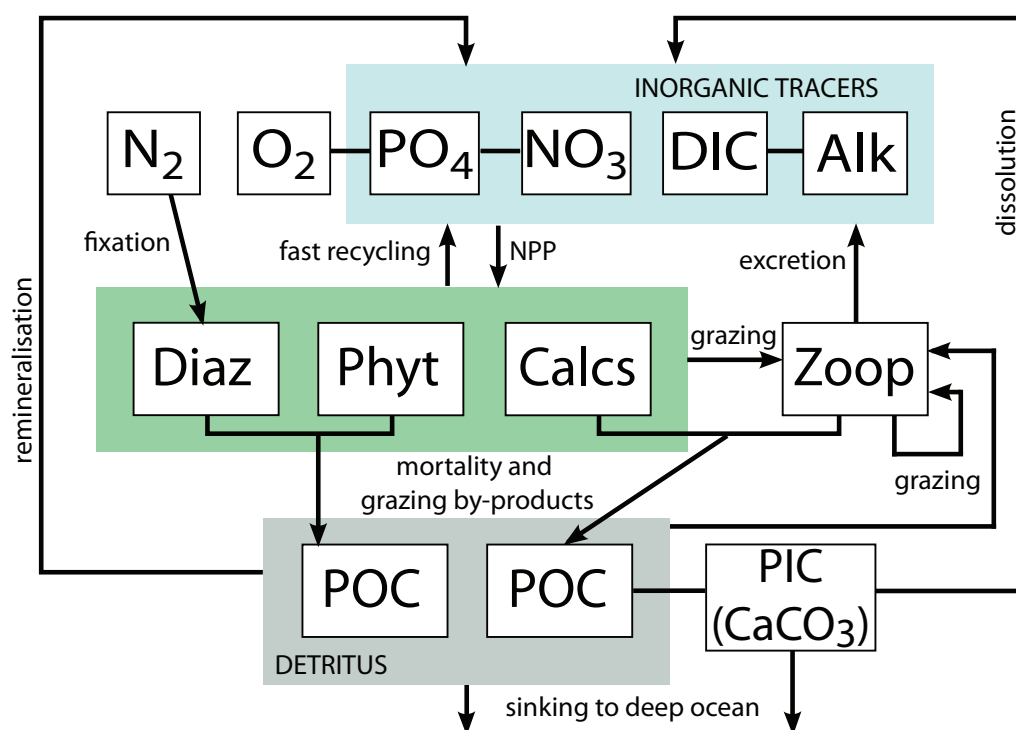


Figure 3.1: UVic ESCM biogeochemical model schematic. Arrows indicate the flux direction of nutrients.

In the following model description, notation will generally follow the symbols used in Keller et al. (2012), with additionally “p” standing for the general phytoplankton PFT, “c” standing for the calcifier PFT, and “z” representing zooplankton when a distinction is necessary. Relevant model parameters are listed in Tables 3.1 to 3.4, with the Keller et al. (2012) model being referred to as NOCAL, and this version referred to as CAL. The model description here covers only the most relevant equations, and equations that have changed in this newest version; please see Keller et al. (2012), Schmittner et al. (2005), and Schmittner et al. (2008) for a complete description of the other equations.

3.1.1 Tracer Equations

Tracer concentrations (C) vary according to:

$$\frac{\partial C}{\partial t} = T + S \quad (3.1)$$

with T including all transport terms (advection, diffusion, and convection), and S representing all source and sink terms. Phytoplankton and calcifier (X representing either) populations are:

$$S(X) = J_X X - G_X - \mu_X^* X - m_X X \quad (3.2)$$

where growth rate (J), mortality (m), and fast recycling (μ^*) terms are described in Section 3.1.3, and losses to zooplankton grazing (G) are described in Section 3.1.4. Diazotroph population follows:

$$S(Diaz) = J_{Diaz} Diaz - G_{Diaz} - m_{Diaz} Diaz. \quad (3.3)$$

Zooplankton population (Z) is calculated as the total available food scaled with a growth efficiency coefficient (ϖ) minus mortality.

$$S(Z) = \varpi \times (G_P + G_C + G_{Diaz} + G_{Detr_{tot}} + G_Z) - m_Z Z^2 - G_Z. \quad (3.4)$$

Detritus sources and sinks now include contributions from calcifiers and are split into “free” and “ballast” pools using a fixed ratio ($R_{bal:tot}$). Ballasted detritus is formed of the protected portion of calcifier and zooplankton grazing and mortality. This protected portion does not interact with nutrient pools directly, and instead transfers from the “ballast” to “free” detrital pool at the rate of CaCO_3 dissolution (λ , Equation 3.18):

$$Detr_{tot} = Detr_{bal} + Detr_{free} \quad (3.5)$$

$$\begin{aligned}
S(Detr_{bal}) = & (1 - \gamma)[G_{Detr_{bal}} + (G_Z + G_C)R_{bal:tot}] \\
& + (m_Z Z^2 + m_C C)R_{bal:tot} - G_{Detr_{bal}} \\
& - \frac{R_{bal:tot}\lambda\text{CaCO}_3}{R_{\text{CaCO}_3:\text{POC}}R_{\text{C:N}}} - w_C \frac{\partial Detr_{bal}}{\partial z}
\end{aligned} \tag{3.6}$$

$$\begin{aligned}
S(Detr_{free}) = & (1 - \gamma)[G_P + G_{Diaz} + G_{Detr_{free}} + G_Z(1 - R_{bal:tot}) + G_C(1 - R_{bal:tot})] \\
& + m_P P + m_{Diaz} Diaz + m_Z Z^2(1 - R_{bal:tot}) + m_C C(1 - R_{bal:tot}) \\
& - \mu_D Detr_{free} - G_{Detr_{free}} + \frac{R_{bal:tot}\lambda\text{CaCO}_3}{R_{\text{CaCO}_3:\text{POC}}R_{\text{C:N}}} - w_D \frac{\partial Detr_{free}}{\partial z}
\end{aligned} \tag{3.7}$$

where γ is the food assimilation efficiency, $R_{\text{CaCO}_3:\text{POC}}$ is a fixed production ratio of CaCO_3 and detritus, $R_{\text{C:N}}$ is a Redfield molar ratio, and μ_D is the detrital remineralisation rate. As in Keller et al. (2012), detritus is exported from the surface with a sinking speed ($w_{D\text{or}C}$) that increases linearly (in per second units) with depth:

$$w_C = w_{C0} + 5.0e^{-2} \times z \tag{3.8}$$

$$w_D = w_{D0} + 2.0e^{-2} \times z. \tag{3.9}$$

The initial surface sinking speeds of POC and CaCO_3 ($w_{D\text{or}C0}$) are assigned different values to represent the denser structure of CaCO_3 relative to that of POC. Ballasted detritus sinks at the CaCO_3 speed, but once it enters the free pool it uses the detrital sinking speed and remineralisation rate. Any detritus reaching the sediments is dissolved back in to the water column.

Ocean nutrients follow:

$$\begin{aligned}
S(\text{PO}_4^{3-}) = & (\mu_D Detr_{free} + \mu_P^* P + \mu_C^* C \\
& + (\gamma - \varpi)(G_P + G_C + G_{Diaz} + G_{Detr_{free}} + G_Z) \\
& - J_P P - J_C C - J_{Diaz} Diaz) R_{\text{P:N}}
\end{aligned} \tag{3.10}$$

$$\begin{aligned}
S(\text{NO}_3^-) = & (\mu_D Detr_{free} + \mu_P^* P + \mu_C^* C \\
& + (\gamma - \varpi)(G_P + G_C + G_{Diaz} + G_{Detr_{free}} + G_Z) \\
& - J_P P - J_C C - u_N J_{Diaz} Diaz)(1 - 0.8 R_{\text{O:N}} r_{sox}^{\text{NO}_3^-})
\end{aligned} \tag{3.11}$$

where $R_{\text{P:N}}$ and $R_{\text{O:N}}$ are Redfield molar ratios and u_N is the Michaelis-Menten nitrate uptake rate. In suboxic water, oxygen consumption is replaced by the oxidation of nitrate,

$$r_{sox}^{\text{NO}_3^-} = \max\{0, 0.5(1 - \tanh(\text{O}_2 - 8))\} \tag{3.12}$$

$$S(\text{O}_2) = F_{sc} - S(\text{PO}_4^{3-}) R_{\text{O:P}} r_{sox}^{\text{O}_2} \tag{3.13}$$

and ocean surface dissolved oxygen exchanges with the atmosphere (F_{sf_c}). See Equation 3.30 for $r_{sox}^{O_2}$.

DIC and alkalinity tracers are now also a function of sources and sinks of prognostic CaCO_3 (Section 3.1.2):

$$S(\text{DIC}) = S(\text{PO}_4^{3-})R_{\text{C:P}} + \lambda\text{CaCO}_3 - S\text{CaCO}_{3\text{liv}} - [(1 - \gamma)(G_C + G_Z) + m_C C + m_Z Z^2]R_{\text{CaCO}_3:\text{POC}}R_{\text{C:N}} \quad (3.14)$$

$$S(\text{Alk}) = -S(\text{PO}_4^{3-})R_{\text{C:P}} + 2[\lambda\text{CaCO}_3 - S\text{CaCO}_{3\text{liv}}] - 2[(1 - \gamma)(G_C + G_Z) + m_C C + m_Z Z^2]R_{\text{CaCO}_3:\text{POC}}R_{\text{C:N}}. \quad (3.15)$$

3.1.2 Calcite Production and Export

The original model fixed CaCO_3 production to POC using a uniform ratio of CaCO_3 production to non-diazotrophic POC (detritus) production ($R_{\text{CaCO}_3:\text{POC}}$). The CaCO_3 produced then contributed to dissolved inorganic carbon (DIC) and alkalinity with a fixed remineralisation profile dependent exponentially on depth. In our model, the general phytoplankton PFT no longer contributes to CaCO_3 and is instead replaced with the calcifier PFT. Different $R_{\text{CaCO}_3:\text{POC}}$ values for zooplankton and calcifiers can be assigned in the case that the ballast model is turned off, but a second ballasted detritus tracer would be required for this feature to be used with the ballast model. This second detritus tracer is not yet implemented, so the tuned model presented here includes ballast and a shared $R_{\text{CaCO}_3:\text{POC}}$ value for zooplankton and phytoplankton calcifiers. In earlier versions of the UVic ESCM, a $R_{\text{CaCO}_3:\text{POC}}$ value of 0.03 was used. In this version, it is increased to 0.04 since the overall calcifying biomass has decreased, which places it closer to (but still outside of) the low end of the 0.05–0.25 range estimated by others and summarised by Fujii et al. (2005). A $\text{CaCO}_3:\text{POC}$ production ratio for *E. huxleyi* is summarised by Paasche (2001) to vary between 0.51–2.30. A lower rain ratio for the model therefore indicates the calcifier PFT cannot be considered to represent calcifiers exclusively, with other non-calcifying phytoplankton sharing the physiological traits also represented by the PFT.

CaCO_3 production and dissolution are now a source and sink of a prognostic CaCO_3 tracer (Equation 3.17). Calcite held in living tissue is calculated separately as the net source - sink from calcifiers and zooplankton (Equations 3.2 and 3.4), converted to CaCO_3 units:

$$S\text{CaCO}_{3\text{liv}} = [S(C) + S(Z)]R_{\text{CaCO}_3:\text{POC}} \times R_{\text{C:N}} \quad (3.16)$$

where $R_{C:N}$ is the Redfield ratio (Table 3.1).

New model tracer particulate CaCO_3 (in non-living form) follows the same general model structure as detritus, though the base units are $\text{mmol carbon m}^{-3}$ rather than $\text{mmol nitrogen m}^{-3}$. The source and sink terms for CaCO_3 include both calcifier and zooplankton sources from grazing and mortality, and losses from dissolution and sinking:

$$S(\text{CaCO}_3) = [(1 - \gamma)(G_C + G_Z) + m_C C + m_Z Z^2] R_{\text{CaCO}_3:\text{POC}} R_{C:N} - \lambda \text{CaCO}_3 - w_C \frac{\partial \text{CaCO}_3}{\partial z}. \quad (3.17)$$

A CaCO_3 dissolution rate (λ) that allows for supersaturated dissolution (Milliman et al., 1999) is calculated using a fixed dissolution rate parameter (k), following the calculation used in the PISCES model family (Aumont et al., 2003):

$$\lambda = \min(1, \frac{1 - \delta_{sat}}{k + |\delta_{sat}|}) \quad (3.18)$$

where δ_{sat} is the deviance of the ambient seawater carbonate concentration from saturation ($\delta_{sat} = [\text{CO}_3] - [\text{CO}_3]_{sat}$) and any negative λ is set to zero. Other thermodynamic dissolution parameterisations were tested in sensitivity simulations spanning over 100 different combinations, but none produced realistic alkalinity and DIC profiles without allowing for supersaturated dissolution, and none as successfully as the one shown here.

Particulate CaCO_3 that reaches the sediments accumulates in an oxygen-only respiration model following Archer (1996b). During model spin-up, losses of alkalinity to the sediment model are exactly compensated by a terrestrial weathering flux (diagnosed from the net sediment burial rate) which is applied as a flux of alkalinity to the ocean through river discharge. Once the model is in equilibrium either a constant or a prognostic terrestrial weathering flux anomaly can be used (Meissner et al., 2012).

3.1.3 Phytoplankton

As in Keller et al. (2012), the maximum possible growth rate of phytoplankton and calcifiers ($J_{\max}$) is a modified Eppley curve (Eppley, 1972), and is a function of seawater temperature (T), an e-folding temperature parameter T_b , and iron availability (u_{Fe}). Parameter values are listed in Table 3.3. Calcifiers are assigned a lower maximum growth rate (a) than mixed phytoplankton, an assumption used previously by Le Quéré et al. (2005) but also justified by comparing measured growth rates for a selection of four coccolithophores by Buitenhuis et al. (2008) ($0.3\text{--}1.0 \text{ day}^{-1}$ at

15°C) with the general range for phytoplankton by Eppley (1972) (a maximum rate of about 2.2 day⁻¹ at 15°C).

$$J_{\max} = a \times e^{\frac{T}{T_b}} \times u_{\text{Fe}} \quad (3.19)$$

Iron limitation is calculated from the concentration of iron that is prescribed in interpolated monthly-mean fields using an iron half saturation approximation constant (k_{Fe}) (Keller et al., 2012; Galbraith et al., 2010). Inclusion of a prognostic iron cycle in the UVic ESCM would increase the computational cost of running the model and is outside of the realm of this model development project, though is currently underway (L. Nickelsen, personal communication). However, accounting for iron limitation on growth rates by means of a limitation mask improves phytoplankton biogeography without additional computational cost (Keller et al., 2012). Calcifiers and mixed phytoplankton are assigned different k_{Fe} values that vary the degree of iron limitation, and that are tuned to produce the best possible PFT distributions, not actual iron affinities. Calcifiers are assigned a lower k_{Fe} value than mixed phytoplankton to simulate the relatively low iron half saturation constant for calcifiers recommended by Le Quéré et al. (2005).

$$u_{\text{Fe}} = \frac{\text{Fe}}{k_{\text{Fe}} + \text{Fe}} \quad (3.20)$$

The maximum potential growth rate is then multiplied by a nutrient availability (u) for both nitrate and phosphate to calculate growth under nutrient limitation, where k_{N} and k_{P} are half saturation constants.

$$u_{\text{NO}_3^-} = \frac{\text{NO}_3^-}{k_{\text{N}} + \text{NO}_3^-} \quad (3.21)$$

$$u_{\text{PO}_4^{3-}} = \frac{\text{PO}_4^{3-}}{k_{\text{P}} + \text{PO}_4^{3-}} \quad (3.22)$$

These equations are applied to obtain maximum possible growth rates as a function of temperature and nutrients. As in Schmittner et al. (2005), the maximum possible growth rate under limited light availability (J_I) is calculated as:

$$J_I = \frac{J_{\max} \alpha I}{[J_{\max}^2 + (\alpha I)^2]^{\frac{1}{2}}} \quad (3.23)$$

where α is the initial slope of the photosynthesis versus irradiance (I) curve. Calcifiers have a lower α than diatoms, though it is similar to non-bloom forming mixed phytoplankton (summarised in Le Quéré et al., 2005). Therefore, a lower α value

for calcifiers is used here. Additionally, light scattering by coccoliths is considered in calculating available irradiance at each depth level:

$$I = I_{z=0} \text{PAR} e^{-k_w \tilde{z} - k_c \int_0^{\tilde{z}} (P+C+Diaz) dz - k_{\text{CaCO}_3} \int_0^{\tilde{z}} (\text{CaCO}_3) dz} \cdot [1 + a_i (e^{-k_I (h_i + h_s)} - 1)] \quad (3.24)$$

where PAR stands for the photosynthetically available radiation, k_w , k_c , k_{CaCO_3} , and k_I are the light attenuation coefficients for water, all phytoplankton (calcifiers, diazotrophs, and general phytoplankton), CaCO_3 , and ice, $\tilde{z}$ is the effective vertical coordinate, a_i is the fractional sea ice cover, and h_i and h_s are calculated sea ice and snow cover thickness. Values for k_c and k_{CaCO_3} come from Balch and Utgoff (2009).

The actual growth rate (J_{PorC}) of the general phytoplankton and calcifier PFTs is taken to be the minimum of the three growth functions described above:

$$J_{\text{PorC}} = \min(J_I, J_{\max} u_{\text{NO}_3^-}, J_{\max} u_{\text{PO}_4^{3-}}). \quad (3.25)$$

Diazotroph growth is not dependent on NO_3^- concentration and hence follows:

$$J_{\text{Diaz}} = \min(J_{(\text{Diaz})I}, J_{(\text{Diaz})\max} u_{\text{PO}_4^{3-}}). \quad (3.26)$$

Two loss terms other than predation (which is described below) are considered. Mortality from old age or disease is parameterised using a linear mortality rate (m). Temperature-dependent fast remineralisation is parameterised using a temperature dependency multiplied by a constant (μ_0^*):

$$\mu^* = \mu_0^* \times e^{\frac{T}{T_b}}. \quad (3.27)$$

3.1.4 Grazing

Zooplankton grazing (G) follows Keller et al. (2012). Relevant parameters are listed in Table 3.4. Grazing of each food source (mixed phytoplankton, calcifiers, diazotrophs, zooplankton, detritus) is calculated using a Holling II function, where a calculated maximum zooplankton grazing rate ($\mu_Z^{\max}$) is reduced by a scaling that is weighted by a food preference (ψ_X , where “X” stands for any of general phytoplankton, calcifiers, diazotrophs, zooplankton or total detritus), the total prey population and a half saturation constant for zooplankton ingestion (k_z):

$$G_X = \mu_Z^{\max} \times Z \times X \frac{\psi_X}{P + C + Diaz + Detr_{\text{tot}} + Z + k_z}. \quad (3.28)$$

The calculated maximum potential grazing rate is a function of a maximum potential grazing rate at 0°C (μ_Z^θ), temperature, and oxygen, where grazing activity is capped

when temperatures exceed 20°C:

$$\mu_Z^{\max} = \mu_Z^{\theta} \times \max \left\{ 0, r_{sox}^{O_2} \times b^{c \cdot \min(20, T)} \right\}. \quad (3.29)$$

Grazing is also reduced under hypoxic conditions ($r_{sox}^{O_2}$):

$$r_{sox}^{O_2} = 0.5(\tanh(O_2 - 8) + 1) \quad (3.30)$$

where O_2 is dissolved oxygen in μM .

3.2 Model Tuning

Model tracers alkalinity and DIC are very sensitive to the prognostic CaCO_3 described in the previous section, which made model tuning a challenge. Stabilising the model with realistic parameter values required multiple steps. After each step, conservation of global alkalinity and carbon was confirmed before proceeding. The original UVic ESCM ocean chemistry is in fairly good agreement with observations, so the initial goal was to tune the model as closely as possible to the original version. To do this, annual mean CaCO_3 dissolution at a pre-industrial equilibrium was diagnosed from the original model. The output file was then fed into the new model (but, for structural reasons, without the ballast model turned on) to prescribe CaCO_3 dissolution. CaCO_3 production in the new model was not dramatically changed from the original model, but the possibility of greater dissolution than production plus transport into any given grid box meant a correction term was required to avoid negative CaCO_3 concentrations. The CaCO_3 tracer was therefore calculated from the ocean bottom to the surface in a reverse depth loop, where if the tracer was calculated as negative, a correction term was added to the concentration to set the tracer equal to zero. The correction term was then carried in to the tracer calculation in the grid box above, which was likewise adjusted with a correction term if needed (basically changing the sinking speed). At the surface, the integrated correction was added to the total CaCO_3 production to conserve carbon. In this way, the new model with a prognostic CaCO_3 tracer was able to reproduce the alkalinity and DIC fields of the original instant-export-production model.

The next step was to tune production as closely as possible to average global estimates and PFT distributions in the modern ocean. Production parameters have been shown to be highly model-dependent (Kriest and Oschlies, 2011). Parameters were adjusted under the constraints that mixed phytoplankton parameters be kept at original model parameter values, and that calcifier growth rate, N and Fe uptake and α values would all be lower than the mixed phytoplankton parameter values

Table 3.1: Miscellaneous UVic ESCM biogeochemical model parameters. Temperature-dependent parameter values are given for 0°C.

Parameter	Symbol	Units	NOCAL	CAL	Published range or synthesised value
Diazotroph growth handicap	c_D	unitless	0.4	0.4	
E-folding temperature	T_b	°C	15.65	15.65	
Detrital remineralisation rate	μ_{D0}	day ⁻¹	0.055	0.055	0.02–0.1 ^a
Detrital sinking speed at surface	w_{D0}	m day ⁻¹	14.0	14.0	10–50 ^b
Ballast:Total detrital production ratio	$R_{bd:tot}$	unitless	N/A	0.05	0.075 ^c
Molar organic P:N ratio	$R_{P:N}$	unitless	0.0625	0.0625	
Molar organic C:N ratio	$R_{C:N}$	unitless	6.625	6.625	
Molar organic O:N ratio	$R_{O:N}$	unitless	10.0	10.0	

^a Summarised in Sarniento and Gruber (2006).

^b From Berelson (2001).

^c From Klaas and Archer (2002).

Table 3.2: UVic ESCM model CaCO_3 export-production parameters.

Parameter	Symbol	Units	NOCAL	CAL	Published range or synthesised value
CaCO_3 :POC production ratio	$R_{\text{CaCO}_3:\text{POC}}$	unitless	0.03	0.04	$0.05\text{--}0.25^a$
CaCO_3 dissolution half saturation constant	k	mmol C m^{-3}	N/A	100	100^b
CaCO_3 sinking speed	w_{CO}	m day^{-1}	N/A	35	50.0^b
Light attenuation by CaCO_3	k_{CaCO_3}	$(\text{m mmol m}^{-3})^{-1}$	N/A	0.47	$1.19^*k_w^c$

^a Summarised in Scott et al. (2011).

^b From PlankTOM10 but originating in PISCES Aumont et al. (2003).

^c Where k_w is the light attenuation of water. From Balch and Utgoff (2009).

Table 3.3: UVic ESCM biogeochemical model phytoplankton production parameters. Temperature-dependent parameter values are given for 0°C.

Parameter	Symbol	Units	NOCAL	CAL	Published range or synthesised value
Maximum growth rate	a_P	day ⁻¹	0.6	0.6 ^a	0.01–5.1 ^{b,c}
	a_C		N/A	0.52	0.91–1.20 ^d
Half-saturation constant N	k_{NP}	mmol m ⁻³	0.7	0.7	0.001–0.85 ^{b,c}
	k_{NC}		N/A	0.4	0.15–0.21 ^d
Half-saturation constant Fe	k_{FeP}	mmol m ⁻³	0.1 ^e	0.1	0.00002 ^a
	k_{FeC}		N/A	0.06	0.00002 ^a
	k_{FeDiaz}		0.1	0.12	0.00012 ^a
Initial slope of P-I curve	α_P	(W m ⁻²) ⁻¹ d ⁻¹	0.1	0.1	0.046–2.40 ^{b,c}
	α_C		N/A	0.06	0.06 ^a
Light attenuation by phytoplankton	k_c	(m mmol m ⁻³) ⁻¹	0.47	0.43	1.08* k_w ^f
Phytoplankton mortality rate	m_P	day ⁻¹	0.03	0.03	0.008–0.25 ^{b,c}
	m_C		N/A	0.03	0.05 ^a
	m_{Diaz}		0.015	0.015	0.05 ^a
Microbial fast recycling	μ_{0P}^*	day ⁻¹	0.015	0.015	0.05 ^a , 0.00–0.025 ^{b,c}
	μ_{0C}^*		N/A	0.015	0.16 ^d

^a From Le Quéré et al. (2005).

^b Summarised in Scott et al. (2011).

^c Range is general and does not distinguish by PFT.

^d Summarised in Litchman et al. (2006).

^e UVic ESCM value is tuned to an iron mask and is not the actual physiological iron limitation (Keller et al., 2012).

^f Where k_w is the light attenuation of water. This is a high-end estimate from Balch and Utgoff (2009).

Table 3.4: UVic ESCM biogeochemical model zooplankton parameters. Temperature-dependent parameter values are given for 0°C.

Parameter	Symbol	Units	NOCAL	CAL	Published range or synthesised value
Maximum grazing rate	μ_Z^θ	day ⁻¹	0.4	0.4	0.06–2.0 ^a
Maximum grazing rate parameters	b	unitless	1.066	1.066	
	c	°C ⁻¹	1.0	1.0	
Food preferences	ψ_P	unitless	0.30	0.225	$\psi_P < \psi_C^{b,c}$
	ψ_C		N/A	0.225	
	ψ_Z		0.30	0.225	
	ψ_{Diaz}		0.10	0.1	
	$\psi_{Detritot}$		0.30	0.225	
Half saturation constant	k_z	mmol m ⁻³	0.15	0.15	0.4–1.0 ^a
Growth efficiency constant	ϖ	unitless	0.4	0.4	0.2–0.4 ^d
Assimilation efficiency	γ	unitless	0.7	0.7	0.46–0.95 ^{a,c}
Mortality rate	m_z	day ⁻¹	0.06	0.06	0.03–0.2 ^a

^a Summarised in Scott et al. (2011).

^b Summarised in Litchman et al. (2006).

^c Model-derived.

^d Summarised in Stock and Dunne (2010).

(Le Quéré et al., 2005). According to Scott et al. (2011), over 10% of model variance in primary production is attributable to four parameters: maximum growth rate (a , in the high and mid-latitudes), the initial slope of the photosynthesis-irradiance curve (α , at all latitudes), mortality (a more model-dependent variable having the largest impact at low latitudes, μ_0^* and μ_0 here), and the carbon to chlorophyll ratio (at low latitudes, but not included in this model). Growth rate was by far the most sensitive of the production parameters in this model, with mortality and α holding less of an influence on biomass and biogeography. As has been shown previously (e.g. Cropp and Norbury, 2009), achieving multiple extant PFTs required careful model tuning. Nutrient half saturation constants for nitrate and iron provided calcifiers a competitive advantage, while a lower growth rate and α produced a disadvantage. The tuning of these parameters required an iterative process to “balance” the relative advantages with the relative disadvantages enough that both general phytoplankton and calcifier populations remained extant, and roughly realistically distributed in the surface ocean. As in other multiple-PFT models (e.g., Cropp and Norbury, 2009) similar growth rates for calcifiers and general phytoplankton were required to maintain both populations, but more variable nutrient uptake and grazing parameter values were possible.

With fixed CaCO_3 dissolution, tuned production, and stable alkalinity and DIC, the next step was to tune the CaCO_3 sinking rate. A sensitivity study across a range of w_{C0} and $R_{\text{CaCO}_3:\text{POC}}$ values was conducted to determine what combination yielded the best fit to the original model CaCO_3 export, and did not substantially alter ocean alkalinity distributions. After these parameter values were determined, the model was integrated for several thousand years to achieve an equilibrated state. The new model CaCO_3 dissolution scheme was run in parallel as a diagnostic only, and roughly tuned to match the original model dissolution. The new model CaCO_3 dissolution scheme replaced the original dissolution scheme after model equilibrium was achieved. The reverse-loop correction of CaCO_3 was not necessary after this step, and so it was turned off and CaCO_3 was treated like any other tracer in the model.

CaCO_3 ballasting of detritus was the last component of the model to be turned on. Parameters $R_{\text{bal:tot}}$, w_{D0} , w_{C0} , and $R_{\text{CaCO}_3:\text{POC}}$ were then re-evaluated to determine the optimal values. Altogether, over two thousand test runs were required to achieve a tuned model.

3.3 Model Assessment

For the purpose of evaluation, the NOCAL and CAL versions of the model (from Keller et al., 2012, and the one described here) were first brought to pre-industrial equilibrium using a fixed atmospheric CO₂ concentration of 283 ppm over ten thousand year integrations. In each case the same physical parameters are used, and the sediment model is coupled in both integrations (it was not included in the study by Keller et al. 2012).

Model CAL biogeochemical tracers averaged globally and by ocean basin reveal generally improved performance with respect to NOCAL in reproducing Global Data Analysis Project (GLODAP) and World Ocean Atlas (WOA) observations (Key et al., 2004; Garcia et al., 2009, Figures 3.2 and 3.3). This may be partly due to the application of a parameter set in NOCAL that was tuned by Keller et al. (2012) to a model that did not include sediments, while the parameter set in CAL is tuned to achieve the best fit including sediments. Both CAL and NOCAL perform well globally and in the Pacific and Southern Oceans, with larger differences in the Indian and Atlantic basins. Globally integrated biogeochemical properties for CAL and NOCAL (Table 3.5) reveal that while both model versions calculate global net primary production (NPP) within observational range, much of the production occurs in the eastern Pacific and Indian Oceans (right-most panels of Figure 3.4). High production in these regions is primarily from the general phytoplankton PFT in both CAL and NOCAL (panels A and E in Figure 3.4), though calcifiers offer an important contribution in the CAL model (panel B in Figure 3.4). High production in the Indian basin can explain generally low surface nutrient concentrations in this region (Figures 3.5 to 3.7). In the Atlantic, the model performs well with respect to observations of PO₄³⁻ and DIC. As with earlier model versions (e.g., Eby et al., 2009), the most notable discrepancy between Atlantic observations and model results is in surface alkalinity concentrations (Figure 3.7), in which model alkalinity is too low in the Northern Hemisphere mid-latitudes and tropics. Surface DIC in the Western Pacific is improved in the CAL version compared to earlier versions (not shown), though DIC in this region remains too low with respect to observations (Figure 3.6) because of high model NPP.

CAL CaCO₃ concentration peaks in latitudinal bands centred on 50°N, the Equator, and 40°S (Figure 3.8). Limited data exist for this key model variable. Comparison to the Aqua MODIS standard CaCO₃ satellite product (NASA, 2013) reveals large differences between model predicted and satellite concentrations, with the majority of CAL CaCO₃ occurring at low latitudes (because of high NPP) not

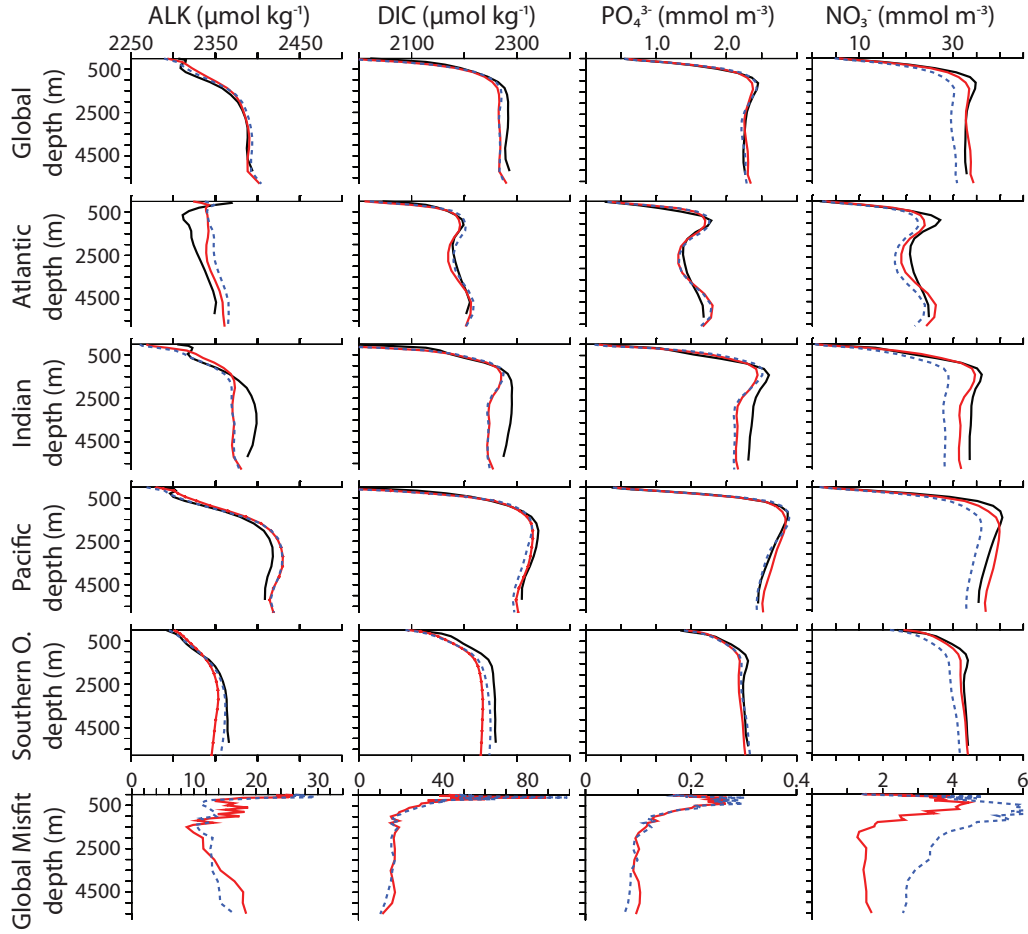


Figure 3.2: Averaged biogeochemical simulated tracers (CAL, red solid line; NO-CAL, blue dashed line) compared to observations (black line). DIC and alkalinity observations are the standard GLODAP product (Key et al., 2004). Phosphate and nitrate observations are annual averages from the World Ocean Atlas (WOA; Garcia et al., 2009). Bottom row shows globally averaged model-data misfits.

Table 3.5: Globally integrated biological properties.

Property	NOCAL	CAL	Independent Estimate
Primary Production (Pg C y ⁻¹)	61.82	64.19	44–78 ^a
Export production at 130 m (Pg C y ⁻¹)	7.77	7.09	5.73 ^b
POC flux at 2 km (Pg C y ⁻¹)	0.26	0.36	0.43 ± 0.05 ^b
CaCO ₃ export at 130 m (Pg C y ⁻¹)	0.94	0.83	1.1 ± 0.3 ^c
CaCO ₃ flux at 2 km (Pg C y ⁻¹)	0.55	0.43	0.41 ± 0.05 ^b
CaCO ₃ dissolution (Pg C y ⁻¹)	N/A	0.40	0.5 ± 0.2 ^d
CaCO ₃ sediment flux (Pg C y ⁻¹)	0.48	0.42	0.21–0.27 ^e
Total Phytoplankton (Pg C)	0.52	0.47	0.5–2.4 ^f
Calcifiers (Pg C)	N/A	0.15	0.001–0.03 ^g
Zooplankton (Pg C)	0.55	0.59	0.03–0.67 ^g

^a Low value from Carr et al. (2006), high value from Jin et al. (2006). Buitenhuis et al. (2013b) recently used a model-data synthesis to constrain the value to 56 Pg C y⁻¹.

^b From Honjo et al. (2008).

^c From Lee (2001).

^d From Feely et al. (2004).

^e 0.1–0.14 Pg C y⁻¹ in pelagic zones, 0.11–0.13 Pg C y⁻¹ in coastal zones, from Iglesias-Rodríguez et al. (2002b).

^f Total global autotrophic biomass from Buitenhuis et al. (2013a).

^g From Buitenhuis et al. (2013a).

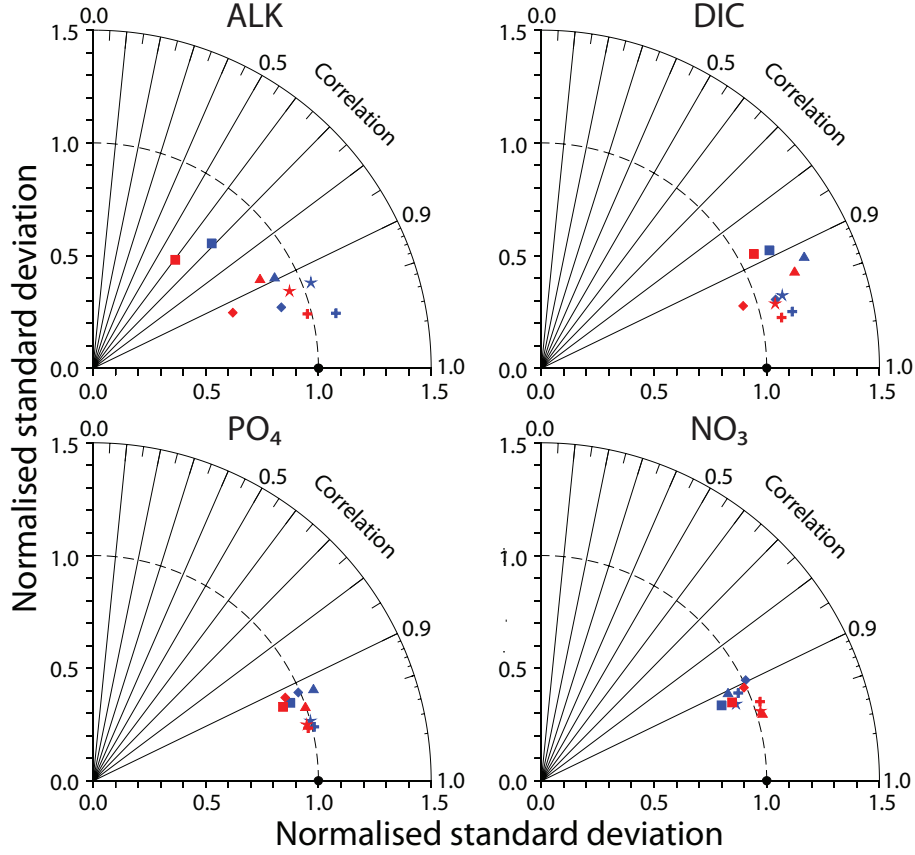


Figure 3.3: Normalised Taylor diagrams of simulated tracers (CAL, red symbols; NOCAL, blue symbols) compared to observations (black circle). Observations used are the same as Figure 3.2. Ocean basins are denoted as: global average (star), Atlantic (square), Indian (triangle), Pacific (plus), and Southern Ocean (diamond).

represented in the satellite product. Lower CaCO_3 estimates by the model at high latitudes are the result of calcifiers being out-competed by the faster-growing general phytoplankton PFT, as well as the model not simulating bloom dynamics. Inclusion of silica limitation for the mixed phytoplankton at the high latitudes would likely increase calcifier populations as well. Satellite data must be used with caution, as they have seasonal bias, do not distinguish between living and dead CaCO_3 (Tyrrell and Merico, 2004) and can overestimate CaCO_3 by 2 to 3 times (Balch et al., 2011). Furthermore, Brown and Yoder (1994) estimate subpolar blooms captured by satellite might only represent 0.3% of the total global calcification, with the majority of coccoliths appearing in sediments having a source that is not detectable with satel-

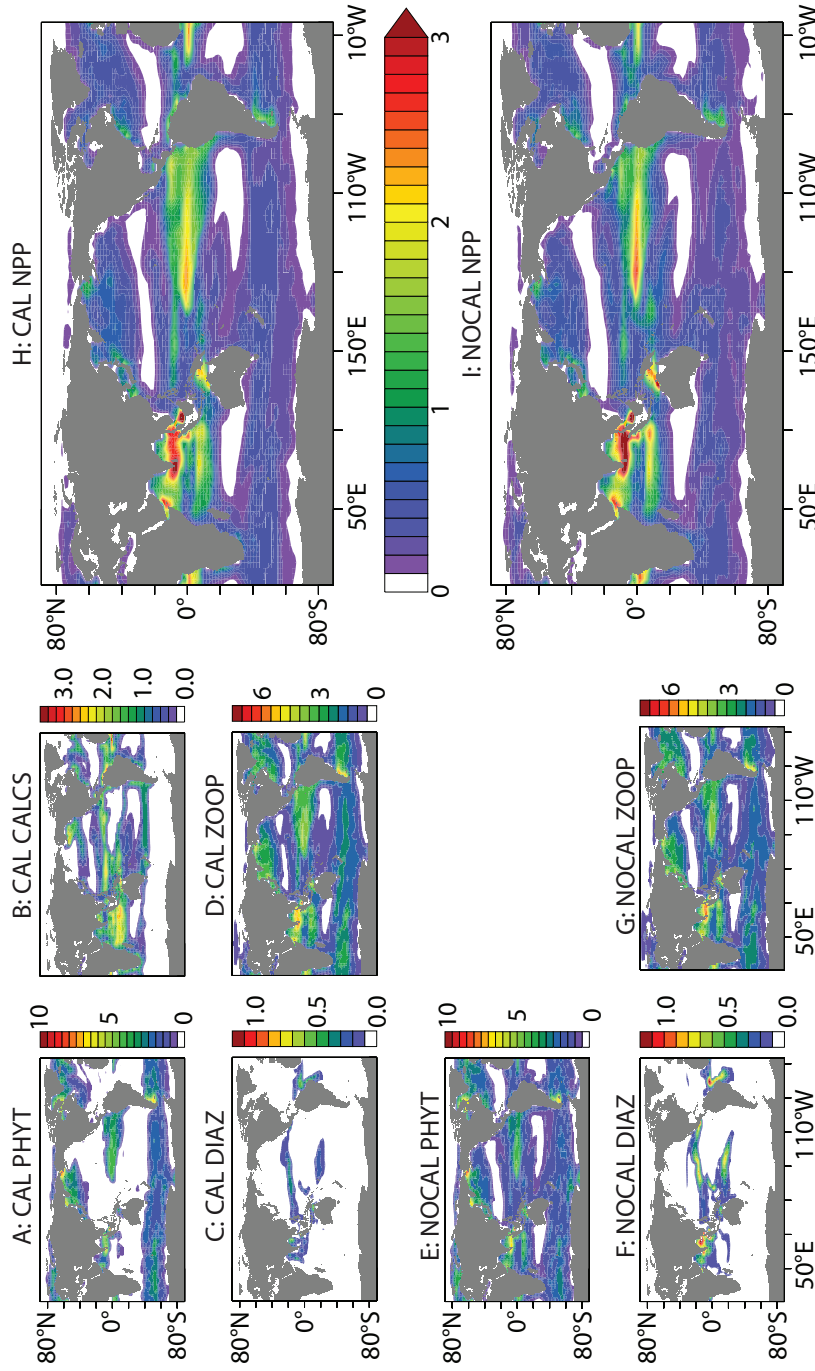


Figure 3.4: Depth-integrated annual average PFT biomass in gC m^{-2} (CAL general phytoplankton, panel A; CAL calcifiers, panel B; CAL diazotrophs, panel C; CAL zooplankton, panel D; NOCAL general phytoplankton, panel E; NOCAL diazotrophs, panel F; NOCAL zooplankton, panel G). Also shown is depth integrated NPP in $\text{gC m}^{-2} \text{ day}^{-1}$ for CAL (panel H) and NOCAL (panel I).

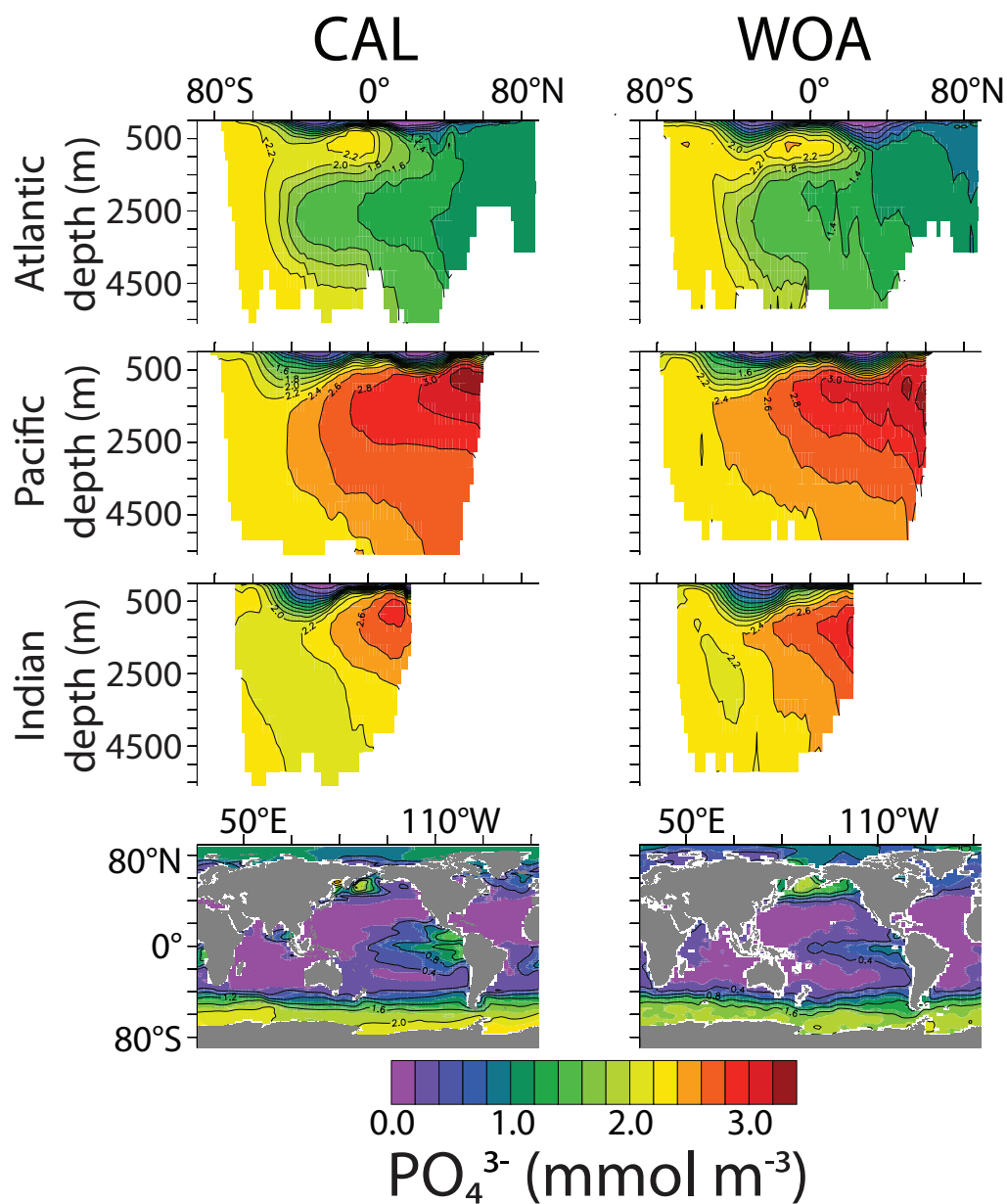


Figure 3.5: Zonally averaged PO_4^{3-} by ocean basin and surface distributions (CAL, left column; WOA observations, right column).

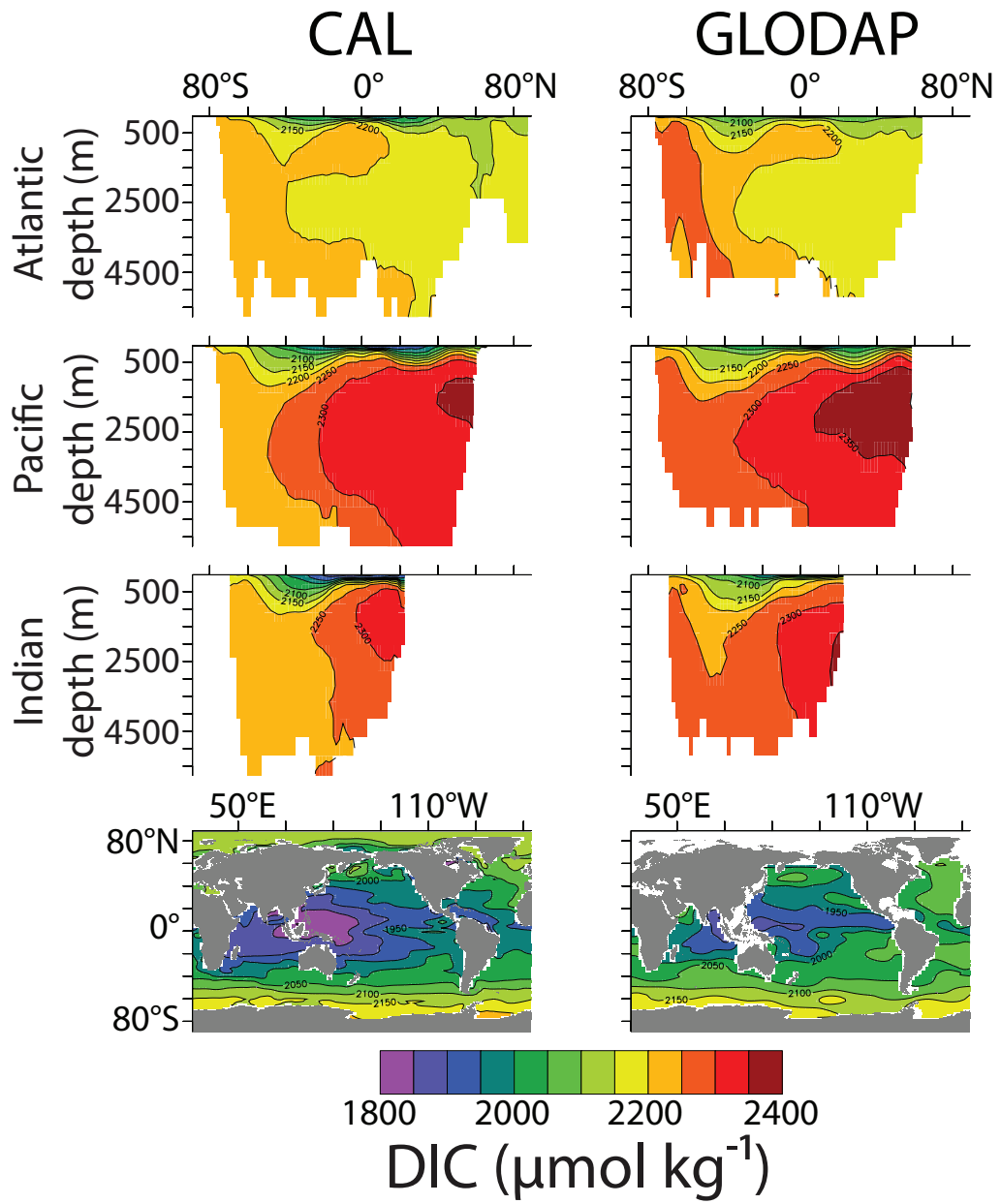


Figure 3.6: Zonally averaged DIC by ocean basin and surface distributions (CAL, left column; GLODAP observations, right column).

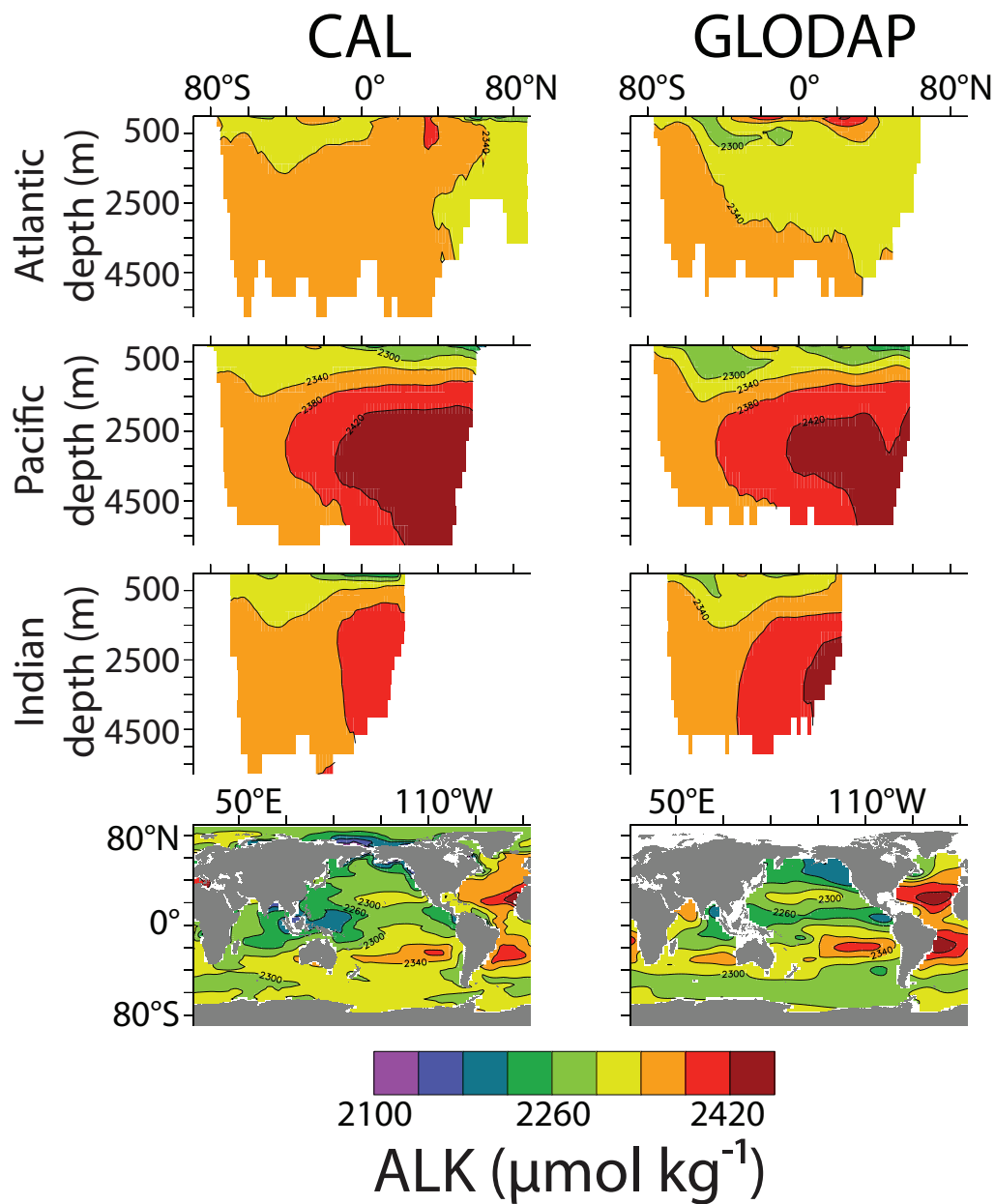


Figure 3.7: Zonally averaged alkalinity by ocean basin and surface distributions (CAL, left column; GLODAP observations, right column).

lites. *In situ* CaCO_3 and POC concentration data are more reliable but sparser. Model living and detached CaCO_3 and POC (detritus and PFT biomass) are used to compare simulated organic and inorganic carbon to *in situ* samples (Figure 3.9). Simulated concentrations of living and detached CaCO_3 are underestimated with respect to the Lam et al. (2011) data compilation for values indicative of blooms (greater than $0.5 \text{ mmol C m}^{-3}$). Simulated CaCO_3 concentrations less than $0.2 \text{ mmol C m}^{-3}$ are overestimated, which is consistent with higher simulated biomass in the low latitudes. A comparison of detached CaCO_3 concentration in CAL with the pre-industrial control concentration of the CMIP5 multi-model ensemble, normalised to the Lam et al. (2011) dataset shows CAL is within the range of CMIP5 models for which these data are available (Figure 3.10), though it is important to note the total comparable data points number less than 1500 for the entire global ocean.

Annually averaged global CaCO_3 export fluxes (Table 3.5 and Figure 3.11) are low compared to sediment trap data from Honjo et al. (2008), though both CaCO_3 and POC fluxes in CAL agree better with observations than those in the NOCAL version (CaCO_3 root mean square error, RMSE, of 147.14 in CAL versus 188.02 in NOCAL, POC RMSE of 97.98 in CAL versus 100.65 in NOCAL, for a sample size of $n = 95$). Improved fluxes are likely due to the addition of the variable dissolution scheme, which calculates a global average dissolution rate of $0.40 \text{ PgC per year}$ (also low but within the range of error when compared to independent estimates, Table 3.5). While application of a ballasting scheme was found to improve POC fluxes, the tuned ballasting parameter $R_{bal:tot}$ yields only a small ballasted POC pool that contributes only 2.6% of the POC reaching the sediments, compared to 80–83% estimated by Klaas and Archer (2002). This result is somewhat interesting in light of Wilson et al. (2012) who propose actual physical ballasting of POC by CaCO_3 might not actually exist. Spatial biases in export fluxes follow those found in CaCO_3 concentration, with too much export in the low latitudes and too little poleward of 60 degrees compared to Honjo et al. (2008). Sarmiento et al. (2002) concluded from a simple box model constrained by global export rates that the major contribution of CaCO_3 to global export must come from low-latitude, non-bloom forming calcifiers or zooplankton, so perhaps the CAL model is performing better than direct comparison to trap and satellite data suggest. Six percent of global total carbon export flux at 50 m depth is CaCO_3 , compared to the Jin et al. (2006) estimate of 4% of the total carbon flux leaving the euphotic zone (75 m depth). Model CAL rain ratio follows the pattern calculated in Sarmiento et al. (2002) of a small POC: CaCO_3 export ratio in the low latitudes that increases poleward.

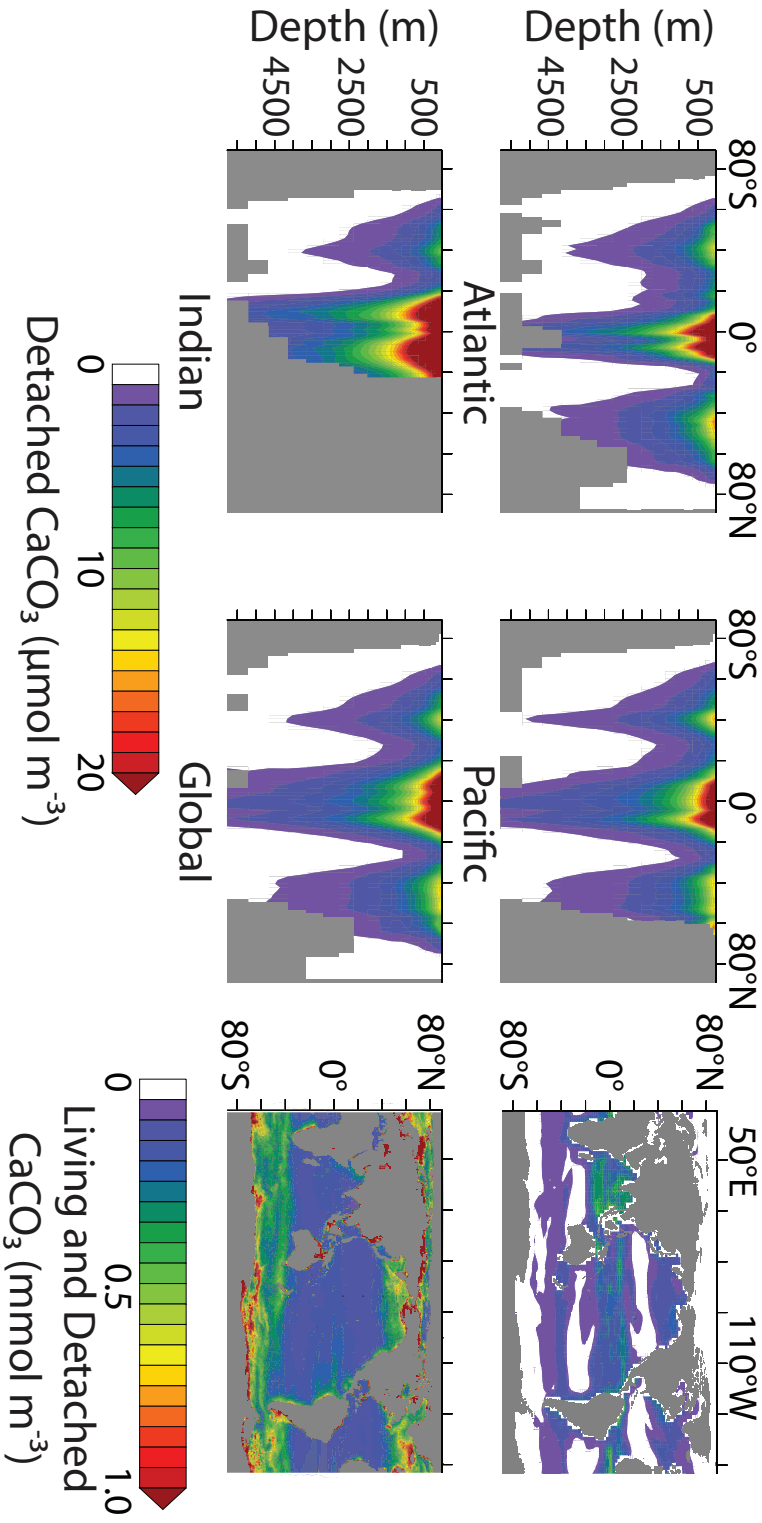


Figure 3.8: Zonally averaged CaCO_3 concentration by ocean basin (left and middle plots). Model CAL CaCO_3 concentration, including living CaCO_3 attached to calcifiers and zooplankton, in the surface grid box (to 50 m depth, top right plot). Bottom right is the standard CaCO_3 product from AQUA MODIS, accumulated over the entire mission (2002–2013, NASA, 2013).

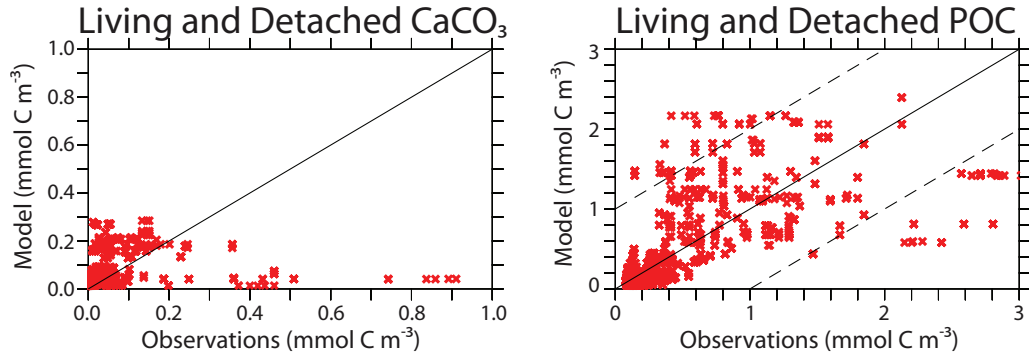


Figure 3.9: Model/observation regression of CAL CaCO_3 concentration (left panel) and CAL POC concentration (right panel) from the ocean surface to 1000 m depth. Data are *in situ* measurements from Lam et al. (2011). Solid line denotes a 1:1 relationship, dotted lines indicate ± 1 .

Simulated sediment composition in CAL has overall lower contributions from CaCO_3 than NOCAL (Figure 3.12). While lower CaCO_3 concentrations represent improvement compared to observational estimates (Archer, 1996a), concentrations are still too high because of the overproduction of calcifiers relative to total production, and the absence of other diluting material in the model.

Unlike earlier versions of the UVic ESCM that used instant export and dissolution, CaCO_3 export now peaks about two months after calcifier biomass reaches seasonal maxima (Figure 3.13, panels A and D). CaCO_3 export is also now lower than in the NOCAL version (Table 3.5 and Figure 3.13, panel E). Model calcifiers bloom too early (March–May, rather than June–July, O’Brien et al. 2013) in the northern latitudes. Zooplankton population in the Northern Hemisphere high latitudes peaks about three months after calcifier biomass, with the seasonal progression being calcifiers first, then general phytoplankton and then zooplankton (Figure 3.13, panels A to C). The model biomass succession is in contrast to the observed diatom to non-diatom progression (e.g., Joint et al., 1993; Riebesell et al., 2007), though without explicit diatoms in the model it is expected that the model ecology could not replicate the behaviour of this keystone PFT. A previously noted correlation between Bering Sea Shelf *E. huxleyi* blooms and seasonal peaks in carbonate ion concentration (Merico et al., 2006) is also not seen in the CAL model because the proposed mechanism (precursor draw-down of DIC by a diatom bloom) is missing. Implementing an explicit dependence for calcifier growth on high CO_3^{2-} would likely shift the calcifier biomass peak several months later in the season and move the gen-

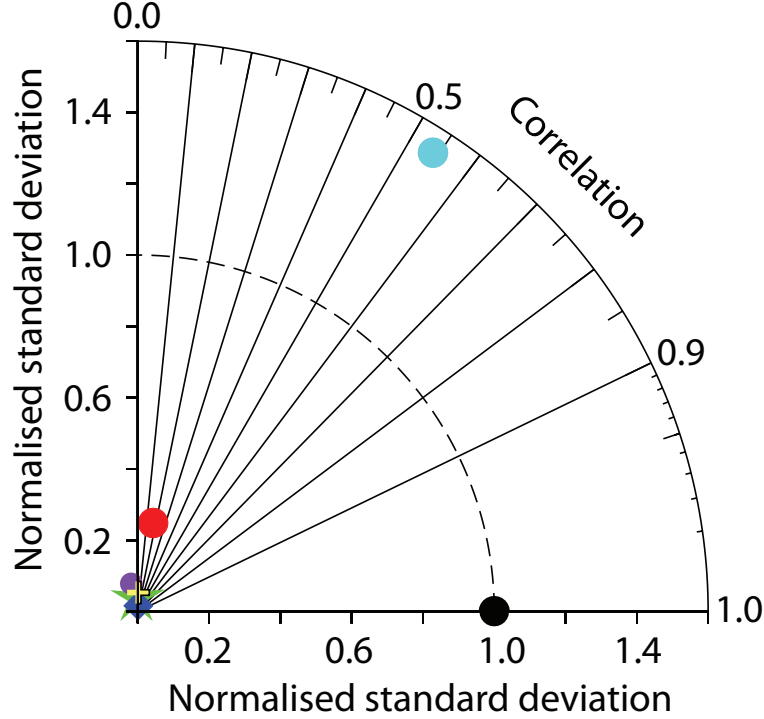


Figure 3.10: Normalised Taylor diagram of model CaCO_3 concentrations compared to the Lam et al. (2011) dataset (black circle). Models are CAL (red circle), GFDL-ES2M (green star), MIROC-ESM (light blue circle), CNRM-CM5 (blue diamond), MPI-ESM-LR (yellow plus), and IPSL-CM5B-LR (purple circle). With the exception of CAL, the data for all models were obtained by mining the CMIP5 database (<http://cmip-pcmdi.llnl.gov>) using the following search terms: CMIP5, ocean biogeochem, pre-industrial control, annual output, calcite concentration.

eral phytoplankton biomass peak forward, possibly improving model performance. Such a dependence might also improve CaCO_3 distributions by reducing the production and export in the low latitude upwelling zones. While increasing calcification correlates with increasing CO_3^{2-} concentrations, no significant correlation between coccolith mass and chlorophyll or cell abundance is apparent in global sampling of surface water and sediment core samples (Beaufort et al., 2011). In the Southern Hemisphere, zooplankton seasonality is the primary driver of CaCO_3 fluxes because of the absence of a model calcifier population south of 40°S .

CAL model calcifiers are reported as a molar concentration, while actual coccolithophores have cell biovolumes (in typical units of μm^3) that are taxonomically

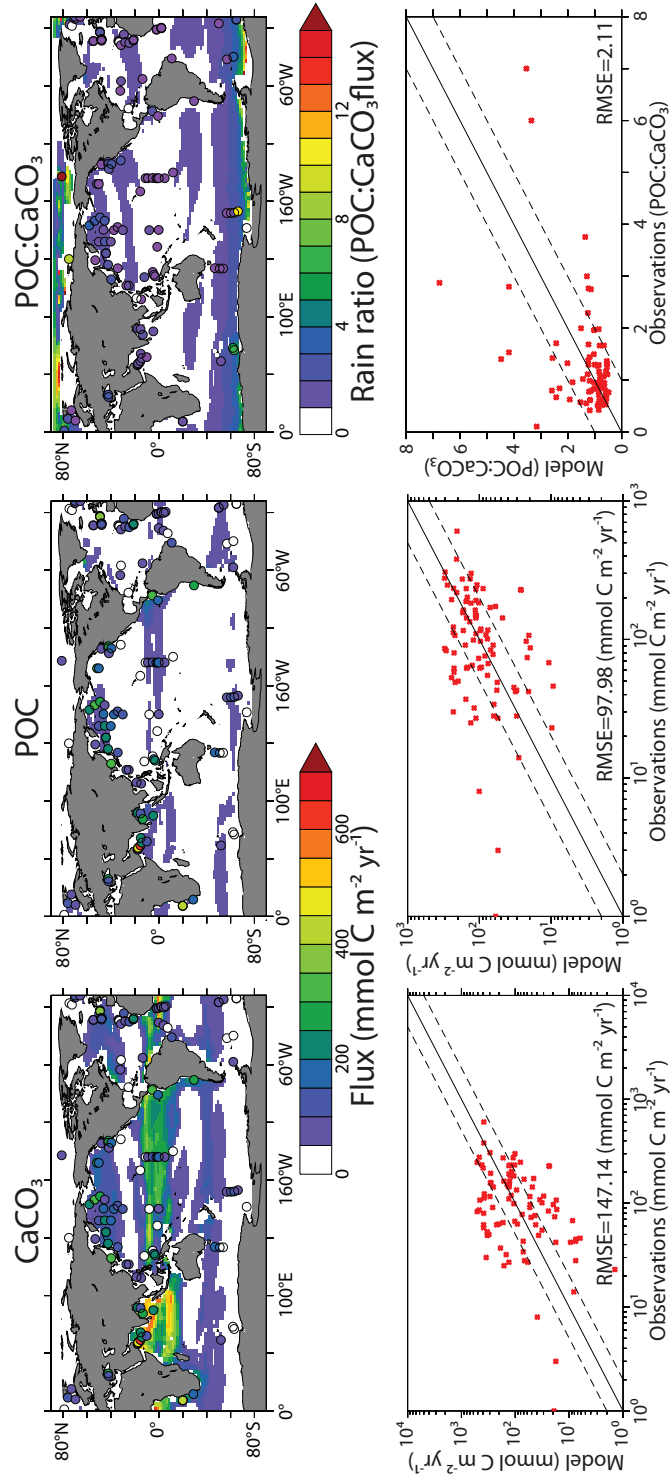


Figure 3.11: Model average CaCO_3 (upper left) and POC (upper middle) export and average POC:CaCO₃ rain ratio (upper right) at 2 kilometers depth overlaid by trap data from Honjo et al. (2008). Model/observation regression in bottom panels.

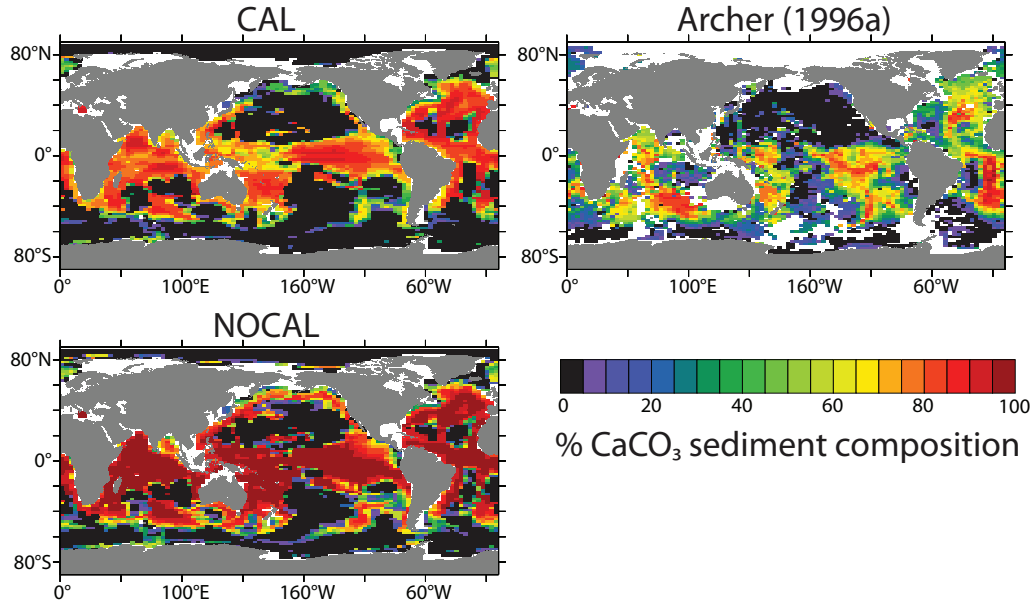


Figure 3.12: Percent CaCO_3 sediment composition. CAL is shown upper left, NOCAL is shown bottom left, and gridded sample data from Archer (1996a) is shown top right.

variable (summarised in O'Brien et al., 2013). Hence predicted calcifier concentrations in the CAL model are more indicative of the presence or absence of the PFT and cannot be expected to reasonably quantify abundance. CAL calcifiers can be compared to the recent Marine Ecosystem Data (MAREDAT) (Buitenhuis et al., 2013a; O'Brien et al., 2013) sample data synthesis. Since the CAL model does not resolve coastal processes, globally integrated total phytoplankton PFT concentrations (Table 3.5) are lower than the MAREDAT estimate. Calcifiers, however, are over-represented by a factor of ten. This overestimate is primarily due to the low number of PFTs in the model, which requires that the calcifier PFT use parameter values (i.e., the growth rate factor) more similar to the general phytoplankton PFT than data support, if it is to avoid extinction. The sparseness of the MAREDAT dataset limits conclusions to noting the CAL model calcifiers have a far greater distribution than what *in situ* sampling supports, and have the highest concentrations in the low latitudes, in contrast to MAREDAT. The discrepancy is mostly due to the overestimate of total production in this region coupled with the necessary over-representation of calcifiers to maintain an extant population. It may also be partly due to the likely sampling bias towards high-latitude blooms in the MARE-

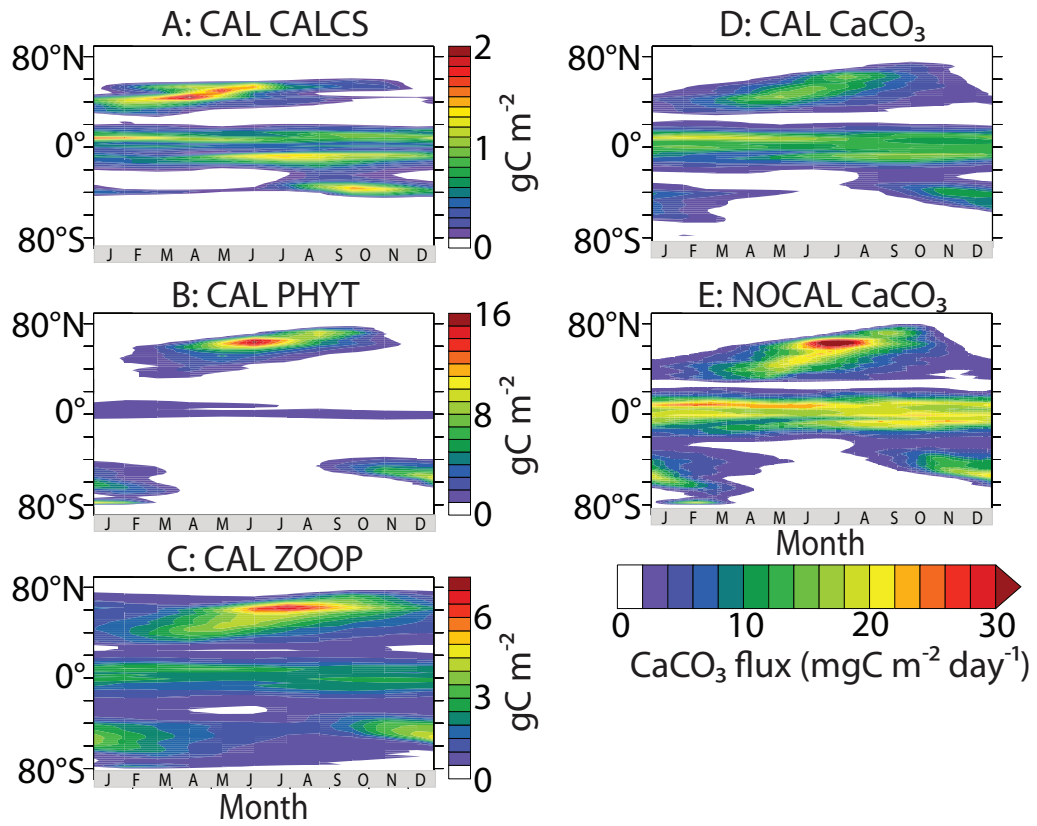


Figure 3.13: Hovmöller diagrams of CAL depth-integrated PFT concentrations by latitude and month (calcifiers, panel A; general phytoplankton, panel B; zooplankton, panel C). Also shown is CaCO_3 flux at 130 m depth by latitude and month for CAL (panel D) and NOCAL (panel E).

DAT synthesis, with lower latitude open ocean regions having relatively few sample points (O'Brien et al., 2013). CAL calcifier biomass maxima in the mid-latitudes (40–60°N, 40°S) are generally consistent with observed high concentrations at 60°N and 20–40°S (O'Brien et al., 2013), and high CaCO_3 export values at 40°N and S calculated by Jin et al. (2006). Also consistent with MAREDAT is the lack of much seasonality in the model Southern Ocean calcifier population, though only calcifying zooplankton are present in this region.

Regional models with multiple PFTs (e.g., Litchman et al., 2006; Tyrrell and Taylor, 1996) or models using nutrient-restoring methods (e.g., Jin et al., 2006) are better able to represent coccolithophore abundances and community composition with data-based (rather than model-based) parameter values; Jin et al. (2006) estimate coccolithophores contributing only 2% of NPP, which is in better agreement with the MAREDAT relative abundance estimate for coccolithophores (Buitenhuis et al., 2013a). Models with fully prognostic PFTs coupled to ocean general circulation models (OGCMs) have a more difficult time reproducing calcifier biogeography and proportionality. Coccolithophores in NASA's biogeochemical model NOBM (five PFTs) (Gregg et al., 2003; Gregg and Casey, 2007) show an overall positive correlation with *in situ* data, though fail to appear in the North Pacific and Antarctic regions. Like the CAL model, coccolithophores in NOBM are over-represented in the Equatorial Pacific (Gregg and Casey, 2007). Though the NOBM coccolithophores contribute more to global NPP (17%) than the Jin et al. (2006) estimate, this is still much less than the CAL model calcifiers' 44% contribution to total NPP. The biogeochemical model PlankTOM5.2 (five PFTs) coupled to two different OGCMs cannot reproduce high-latitude calcifier populations, and mixed phytoplankton and calcifiers do not easily co-exist (Sinha et al., 2010). Also apparent in the coupled PlankTOM5.2–NEMO model is an over-representation of the calcifier population in the Indian and Western Pacific basins (Sinha et al., 2010), which is a problem shared by this model.

Aside from calcifiers, PFT relative concentrations are otherwise in agreement with Buitenhuis et al. (2013a), with diazotrophs having the lowest concentration, followed by general phytoplankton. Diazotroph concentration is substantially lower than the general phytoplankton PFT and is able to remain extant because of its critical advantage of not being nitrogen limited. In CAL as was found by Buitenhuis et al. (2013a), zooplankton concentrations are higher than total phytoplankton concentrations.

As with any model, this one is not without caveats regarding its application. Collapsing complex and poorly understood natural biogeochemical cycles into a

rigid artificial model structure introduces uncertainty into the parameter space of the constructed equations. The degree of under-determination of the model equations is large enough that *a priori* assumptions and optimisation methods have been shown to influence results, with “optimal” parameter values comprising a broad range, each performing equally well with respect to independent data (Ward et al., 2010). It is important to note that while this model has been tuned manually to reduce the model-data error in global state variables, it cannot be considered optimised (Kriest et al., 2010). Furthermore, nutrients to a degree and PFT distributions especially are sensitive to model structure and parameter choice (Anderson et al., 2010; Manizza et al., 2010; Sailley et al., 2013), as well as physical biases in any given ocean model (Doney et al., 2004; Najjar et al., 2007; Sinha et al., 2010). Similarly, models can perform comparatively well for very different structural reasons (Hashioka et al., 2013). It is therefore often difficult to tell if the model is getting the right answer for the wrong reason (e.g. Friedrichs et al., 2007; Sinha et al., 2010). More specifically, biological parameter choice for the calcifying PFT is biased towards *E. huxleyi*, which necessarily biases model results. One must therefore be careful to interpret model results appropriately, given these limitations.

3.4 Conclusions

Calcifying phytoplankton and zooplankton are key components of the ocean carbon cycle and thus their representation in coupled climate models is important for understanding systemic response to change. This model is a unique attempt to include calcifiers as an explicit phytoplankton PFT alongside a general phytoplankton and diazotroph PFT in an intermediate complexity model, and to make the calcifiers and zooplankton responsible for CaCO_3 production and prognostic export, and detrital ballasting. The UVic ESCM now fills a niche in Earth System modelling that was previously unoccupied in that it is relatively inexpensive to run, yet resolves the complete Earth System carbon cycle including prognostic calcium carbonate and a separate calcifier PFT. Since the UVic ESCM includes ocean sediments and calcite compensation (something none of the CMIP5 models do), it is now a model that is particularly well suited to reducing the uncertainty of the fate of emissions over the long term. It is also ideally suited to test the parameter space of feedbacks between the carbonate and carbon cycles and the climate system in transient simulations. The modifications improve the UVic ESCM model’s performance with respect to nutrient distributions and carbon fluxes, and make the model mechanistically more realistic. Primary production, export production, POC and CaCO_3 fluxes at various

depths all fall within independent estimates. While the model is able to reasonably reproduce observed patterns of mid-latitude maximum calcifier concentrations, it also shares biases common to other calcifier PFT models coupled to OGCMs: calcifiers are over-represented in total biomass and at low latitudes, and underrepresented at high latitudes compared to satellite and sample data (Gregg and Casey, 2007; Sinha et al., 2010; Vogt et al., 2013). In the CAL model, failure to resolve coastal processes results in necessarily too-high NPP, CaCO_3 , and POC export-production fluxes in the low latitudes in order to match global estimates. With possibly 48% of total global POC flux occurring in water depths of less than 50 m (Dunne et al., 2007), lacking any sort of parameterisation for these regions imposes a significant bias to the model. In other calcifier multi-PFT models, exact regions of bias are model dependent and attributable to physical and ecosystem differences, but the systematic over-representation of calcifiers in the low latitudes may have some physical justification. Previous studies have shown global export budgets require high CaCO_3 export in this region (Sarmiento et al., 2002), and high latitude bloom CaCO_3 is underrepresented in sediments (Brown and Yoder, 1994). Vogt et al. (2013) noted the similarity of calcifier model biogeography to observed picophytoplankton biogeography, so inclusion of additional picophytoplankton PFTs might improve calcifiers in models.

There are four potential improvements to the CAL model that have not yet been addressed. Simulated calcifiers are wholly dependent on relative competitive advantage, and can easily go extinct or cause the general phytoplankton PFT to go extinct with only small adjustments to production parameter values, especially the growth rate. Because their niche is so poorly defined with respect to the general phytoplankton PFT, additional PFTs (particularly diatoms) are expected to improve their population biogeography, stability, and seasonal behaviour, and may allow calcifier parameter values to become less model- and more data-dependent (though this assumption has not been tested). Secondly, the ballast model does not include a parameterisation for particle aggregation, which would increase the fraction of ballasted POC ending up in the sediments. Thirdly, static stoichiometric ratios in the model ignore their dependence on remineralisation processes (Schneider et al., 2003), carbonate chemistry (Riebesell et al., 2007), biogeography (Weber and Deutsch, 2010), and taxonomy (Arrigo et al., 1999). Including a parameterisation of flexible stoichiometric ratios would have a significant influence on the ecology (Flynn, 2010), nutrient distributions, and carbon uptake (Kortzinger et al., 2001; Schneider et al., 2004). Lastly, the model does not account for decreasing calcification with increasing CO_2 concentration (Riebesell et al., 2000), which would doubtless affect

simulated tracer distributions and biogeography. Furthermore, using a single dissolution parameterisation for zooplankton and calcifier CaCO_3 ignores the likely significant contribution of aragonite dissolution to global alkalinity (Gangstø et al., 2008). These last two were considered for inclusion in this model, but the current code structure is not amenable to flexible or multiple rain ratios, and will require a significant restructuring should these changes be implemented in the future. An alternative to a flexible rain ratio for representing the effect of acidification on production in the calcifier PFT is presented in Chapter 4.

Chapter 4

Application of a Calcite Saturation State Dependency on the Calcifier Population in the UVic ESCM

4.1 Introduction

Calcification of coccolith tests by coccolithophores is a critical biological pathway for atmospheric and ocean carbon into the deep ocean and sediments (Jin et al., 2006; Archer, 1996a), and yet modelling of this pathway presents a challenge because no significant correlation between coccolith mass and chlorophyll or cell abundance is found in global sampling of surface water and sediments (Beaufort et al., 2011). This means that in ocean or earth system models, achieving excellent agreement between coccolithophore biomass *in-situ* data (e.g., O'Brien et al., 2013) and a coccolithophore or calcifier phytoplankton functional type (PFT) does not necessarily produce excellent agreement between CaCO_3 production, concentrations or export, and *in-situ* (e.g., Lam et al., 2011), sediment trap (e.g., Honjo et al., 2008), or satellite (e.g., NASA, 2013) CaCO_3 data.

Coccolithophore calcification does, however, correlate well with carbonate chemistry, specifically $[\text{CO}_3^{2-}]$, $[\text{HCO}_3^-]$, and calcite saturation state (Ω) (Beaufort et al., 2011). This includes not only the absolute mass of the coccolith tests, which increases with increasing Ω , but also in the relative proportion of CaCO_3 in every unit of cell volume (Beaufort et al., 2011). A global survey of ocean samples reveals

this correlation more dramatically than culture experiments, and underscores the role of biodiversity rather than physiology in maintaining the relationship (Beaufort et al., 2011). In general, low $[\text{CO}_3^{2-}]$ (and low Ω) correlates with lesser diversity and lighter coccolith tests, and this relationship is apparent both in the modern ocean as well as in sediment records since the Last Glacial Maximum (Beaufort et al., 2011). This presents a conundrum for biogeochemical modelling, in that while there is no apparent link between calcifier primary production and calcification, clearly there are ecological consequences controlled by carbonate chemistry.

Malformation of coccolith tests in low $[\text{CO}_3^{2-}]$ water might be the relevant effect with ecological consequences. In the Beaufort et al. (2011) analysis, the lightest calcifying *Emiliania huxleyi* coccolithophore morphotype C appeared in very low $[\text{CO}_3^{2-}]$ (less than $200 \mu \text{mol kg}^{-1}$) water with substantial malformations. Increasing coccolith malformation with increasing CO_2 concentrations has also been observed in culture (Riebesell et al., 2000). The physiological function of coccolith tests is uncertain but it can be safely assumed their production provides a benefit that outweighs the cost of production (see review by Raven and Crawford, 2012). To a modeller interested in representing calcification in the global carbon cycle, the specific ecological trade-offs associated with coccolith malformation are probably not as important as capturing the overall effect on net calcifier and calcite production (i.e., changes to the production or loss terms in the population equations).

Glacial-interglacial box model simulations by Omta et al. (2013) suggest explicitly increasing calcifier growth rate with alkalinity improves the simulation of atmospheric CO_2 observed in the ice record and reproduces calcifier population spikes recorded in the sediments. This is the only previous global carbon cycle modelling example to explicitly link carbonate chemistry to calcifier primary production.

4.2 Methods

Though each model is different, the UVic ESCM calcifier source-and-sink equation can illustrate the options available for applying a carbonate chemistry dependency to primary production:

$$S(\text{CALCS}) = J_C \times \text{CALCS} - G_C - \mu_C^* \times \text{CALCS} - m_C \times \text{CALCS} \quad (4.1)$$

where calcifier growth rate (J_C) provides the net source, and mortality (m_C), microbial fast recycling (μ_C^*) and losses to zooplankton grazing (G_C) are the net sink. Scaling terms based on seawater Ω have been applied to the CaCO_3 :POC rain ratio (Ridgwell et al., 2007b; Gehlen et al., 2007; Pinsonneault et al., 2012), with the

Ridgwell et al. (2007b) parameterisation representing a high-end level of sensitivity. The Gehlen et al. (2007) parameterisation was applied to the UVic ESCM by Pinsonneault et al. (2012) previously and is used again here for calcifier production rather than the rain ratio, but modified as:

$$\text{scale} = 1 - \frac{\Omega - 1}{k + (\Omega - 1)} \quad \text{for scale} \geq 0 \quad (4.2)$$

where k is a half-saturation constant. The scaling factor (shown in Figure 4.1) could be multiplied by any of the sink terms in Equation 4.1 (or $[1 - \text{scale}]$ could be multiplied by the source term) to produce an additional cost between zero and one, with decreasing Ω . The following sections describe the results of a sensitivity study using k values of the same range used in the Pinsonneault et al. (2012) study (0.07–20), applied to the growth rate, linear mortality, and microbial fast recycling terms, and present a tuned model using an optimal k value. The scaling factor is not applied to losses from zooplankton grazing because the UVic ESCM is insensitive to grazing preference parameters. Any increase in grazing preference for calcifiers with decreasing Ω (and necessarily, a decrease in grazing preference for mixed phytoplankton) would only have a marginal impact on the biogeography of either PFT. Furthermore, experimental evidence suggests calcifiers, and especially lithed calcifiers, are generally the preferred food of zooplankton (see discussion by Raven and Crawford, 2012).

4.3 Results and Discussion

4.3.1 Growth Rate

Calcifier populations are very sensitive to application of the scaling factor to growth rate $((1 - \text{scale}) \times J_C)$, which reduces or stops production in low- Ω regions such as the Eastern Pacific and high latitudes, and increases production in the low latitude western Pacific and Indian Oceans. As discussed in Chapter 3, the calcifier PFT biogeography in the UVic ESCM CAL model version is determined by calcifier relative fitness compared to the mixed phytoplankton PFT, and is the most sensitive to relative growth rates. Multiplication of the growth rate with the 0 to 1 scaling factor determined by Ω reduces the relative fitness of the calcifier PFT in all regions except those with the highest Ω values, which are also regions generally not inhabited by the mixed phytoplankton PFT because of nutrient limitation. The lack of co-existence of multiple PFTs is a common challenge in ocean models, and the UVic ESCM is no exception to this. Application of the scaling factor to growth rate

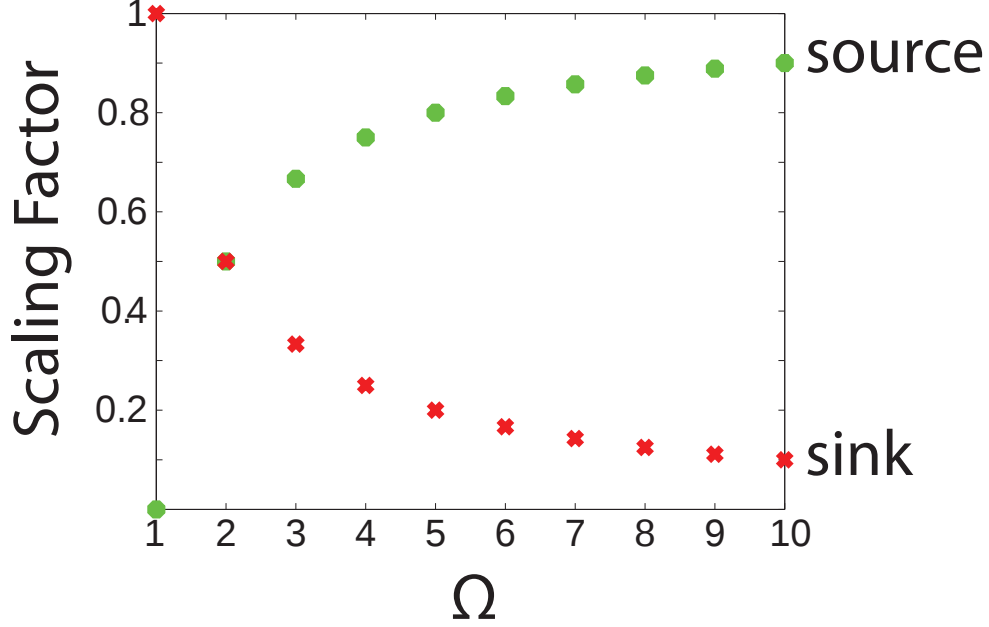


Figure 4.1: Example scaling factor for calcifier population source (green line) and sink (red line) terms, using $k = 1$.

further reduces the co-existence of PFTs and does not improve the calcifier biogeography, particle fluxes, or nutrient distributions. Application of the scaling factor to growth rate is also one of the more dubious parameterisation options because of the aforementioned lack of correlation between calcification and chlorophyll (Beaufort et al., 2011). Of the proposed purposes of coccoliths summarised by Raven and Crawford (2012), those that apply to alleviating light and nutrient limitation (that would consequently increase growth rate) cannot be represented in the UVic ESCM because vertical migration of plankton is not modelled.

4.3.2 Mortality Rate

Mixed phytoplankton populations are very sensitive to application of the scaling factor to the calcifier linear mortality rate ($\text{scale} \times m_C$), and quickly become extinct or nearly extinct for the range of k half-saturation constants used. Since the CAL model uses the same linear mortality rate for both calcifier and mixed phytoplankton PFTs, calcifiers suddenly have a fitness advantage in all regions except where Ω is very low. Application of a higher mortality rate for calcifiers in addition to the scaling factor might improve results of this sensitivity test. Increased mortality of

calcifiers from viruses or old age with decreased Ω is debatable as it appears the calcifier *E. huxleyi* actually succumbs more readily to viruses while in the diploid (coccolith bearing) phase (see discussion by Raven and Crawford, 2012).

4.3.3 Microbial Fast Recycling Rate

Application of the scaling factor to losses from microbial fast recycling ($\text{scale} \times \mu_C^*$) yields the most interesting results. The CAL model applied the same fast recycling parameter value to both calcifiers and mixed phytoplankton, but the calcifier fast recycling term is now reduced with increasing Ω (and calcifiers have a relatively greater competitive advantage everywhere but very low- Ω regions). This scaling implies that calcifiers' tests offer some protection to the calcifier from microbial degradation in moderate to high Ω regions. This protection is lost at low values of Ω , whereupon the calcifiers' vulnerability to microbial degradation is the same as the mixed phytoplankton type.

Application of the scaling factor to microbial fast recycling introduces a large positive feedback for calcifier populations. In well mixed, high nutrient regions that also tend to have lower values of Ω , the mixed phytoplankton PFT dominates in the CAL model because of a faster growth rate advantage. In the new model however, calcifiers now have fewer losses to microbial recycling than mixed phytoplankton, so they become more effective exporters of nutrients from these regions. This lowers the surface nutrient concentrations, which is a relative advantage for the calcifiers, whose population expands. A consequence of the increased calcifier population is increased calcification, which lowers surface Ω values and increases the feedback.

Calcifier competitive advantage is now enhanced relative to mixed phytoplankton in high- Ω regions, though the mixed phytoplankton PFT does not inhabit these regions to begin with because of nutrient limitation. Nutrient limitation becomes more of a problem for the calcifier PFT as reduced microbial recycling reduces surface phosphate and nitrate concentrations. The net result is that low- Ω regions are more favourable to calcifiers, high- Ω regions are less favourable, and global calcifier microbial recycling is lower than in the CAL model (Figure 4.2, where "CAL" is the model described in Chapter 3 and "OMEGA" is the model described here). Mixed phytoplankton distributions have a more diatom-like appearance by moving to the high latitudes, and calcifiers are the dominant PFT (Figure 4.3).

The redistribution of PFTs in OMEGA compared to CAL yields the following biogeochemical modifications, following re-tuning of the model (Table 4.1):

1. Carbon and nutrients compared to data products are only slightly changed,

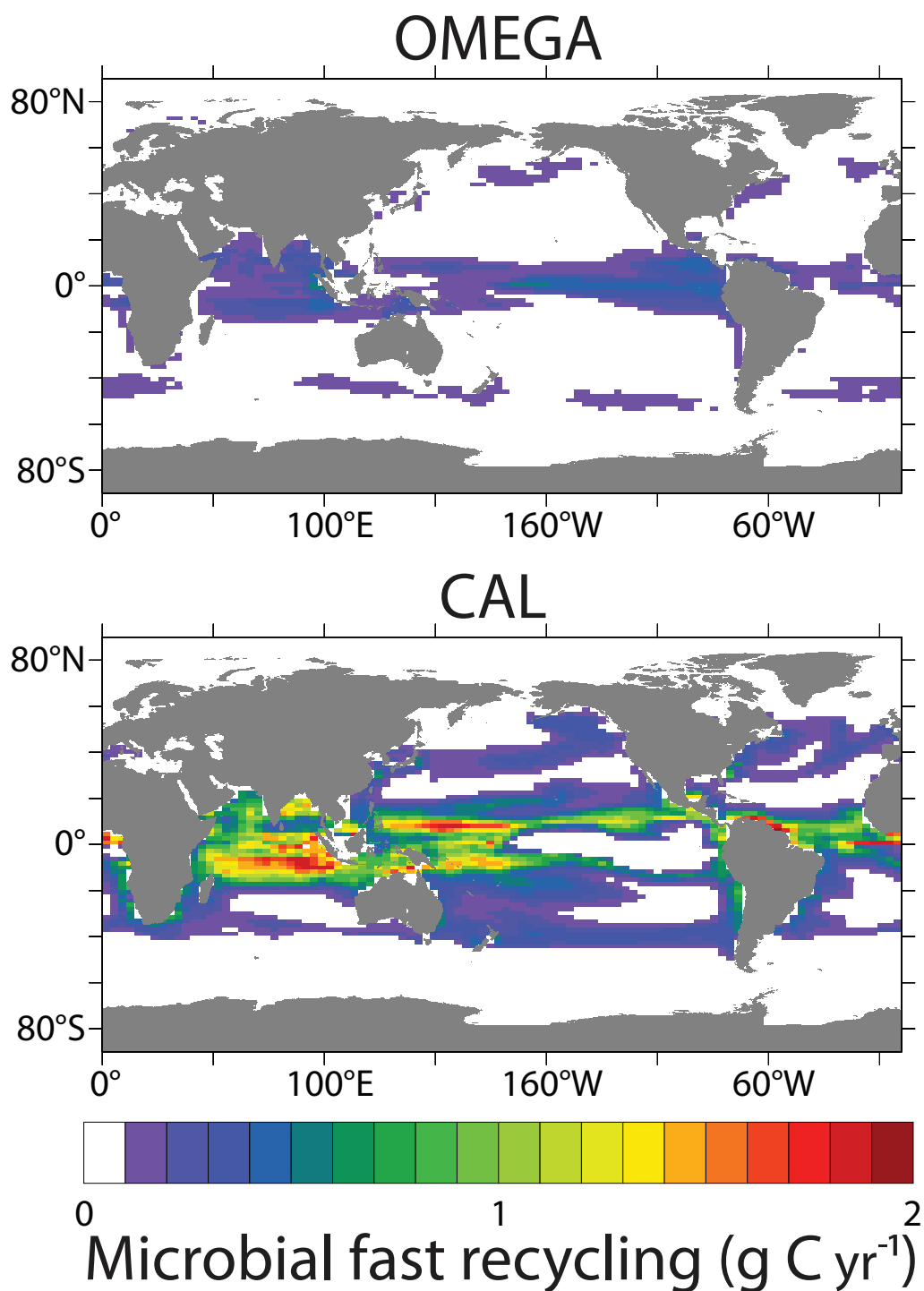


Figure 4.2: Surface microbial recycling of calcifier carbon for OMEGA (top panel) and CAL (bottom panel) configurations.

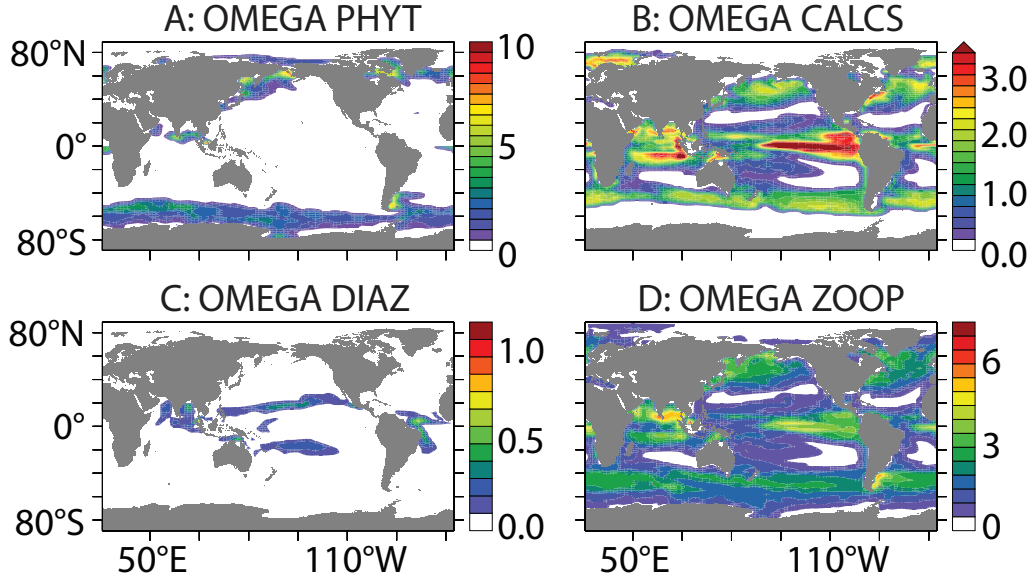


Figure 4.3: Depth-integrated annual average PFT biomass in gC m^{-2} (OMEGA general phytoplankton, panel A; OMEGA calcifiers, panel B; OMEGA diazotrophs, panel C; OMEGA zooplankton, panel D). This figure is comparable to Figure 3.4.

with deep ocean misfits slightly decreased for DIC, slightly increased for PO_4^{3-} and NO_3^- , and mixed for alkalinity (Figure 4.4).

2. Net primary production decreases, though is still within the published range (Table 4.2). Fluxes of organic and inorganic carbon are neither made clearly worse nor improved (Table 4.2 and Figure 4.5). The RMSE is slightly higher for the OMEGA version 2 km depth CaCO_3 and POC fluxes, but the dataset is sparse (only 95 points compared) and certain regions such as the 40°S latitude band and the North Pacific are clearly improved compared to satellite data (Figure 3.8).
3. Calcifier populations are reduced in the western Pacific and Indian Oceans, a region where earth system models typically over-represent calcifier populations (see Figure 4.3 and discussion in Chapter 3). Calcifier populations are increased in the North Pacific, a region where earth system models typically under-represent calcifier populations. Calcifier populations also now exhibit a strong Southern Hemisphere population maximum around 40°S and a greater Southern Ocean presence, which is an improvement over the old model compared to survey data.

Table 4.1: Changed UVic ESCM biogeochemical model parameters.

Parameter	Symbol	Units	CAL	OMEGA
Ω scaling half-saturation constant	k	unitless	N/A	1.0
Ballast:Total detrital production ratio	$R_{bal:tot}$	unitless	0.05	0.04
CaCO ₃ :POC production ratio	$R_{CaCO_3:POC}$	unitless	0.04	0.03
Maximum calcifier growth rate	a_C	day ⁻¹	0.52	0.5

Table 4.2: Globally integrated biological properties.

Property	CAL	OMEGA
Primary Production (Pg C y ⁻¹)	64.19	55.14
Export production at 130 m (Pg C y ⁻¹)	7.09	7.16
POC flux at 2 km (Pg C y ⁻¹)	0.36	0.40
CaCO ₃ export at 130 m (Pg C y ⁻¹)	0.83	0.84
CaCO ₃ flux at 2 km (Pg C y ⁻¹)	0.43	0.47
CaCO ₃ dissolution (Pg C y ⁻¹)	0.40	0.38
CaCO ₃ sediment flux (Pg C y ⁻¹)	0.42	0.45
Total Phytoplankton (Pg C)	0.47	0.39
Calcifiers (Pg C)	0.15	0.27
Zooplankton (Pg C)	0.59	0.59

4.4 Conclusions and Caveats

It has been observed that calcifier organic tissue protects coccolith tests from dissolution, and that this tissue is eroded by heterotrophic microbial activity (see discussion by Raven and Crawford, 2012). Assuming, then, that robust coccolith tests offer a relative fitness advantage, enhanced microbial activity on (or enhanced susceptibility to microbial degradation of) calcifier soft tissue would increase lith dissolution and decrease calcifier relative fitness. So is there evidence of either increased microbial activity or enhanced calcifier bacterial susceptibility with decreasing Ω ? Very little has been published regarding either option. Coccolithophores show rapid adaptability to changing environmental conditions (Lohbeck et al., 2012), which favours the “enhanced microbial activity” over the “enhanced calcifier susceptibility” option. At the same time, particle-associated bacterial communities have been found

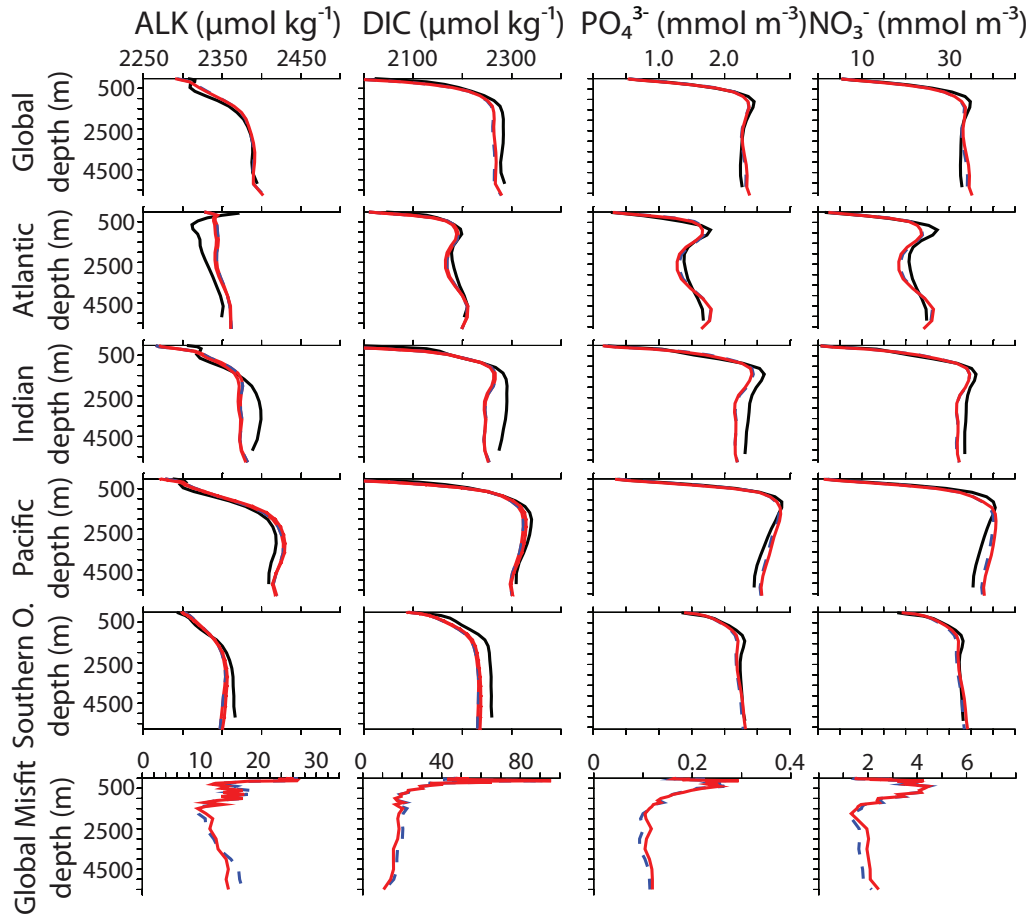


Figure 4.4: Averaged biogeochemical simulated tracers (OMEGA, red solid line; CAL, blue dashed line) compared to observations (black line). DIC and alkalinity observations are the standard GLODAP product (Key et al., 2004). Phosphate and nitrate observations are annual averages from the World Ocean Atlas (WOA; Garcia et al., 2009). Bottom row shows globally averaged model-data misfits.

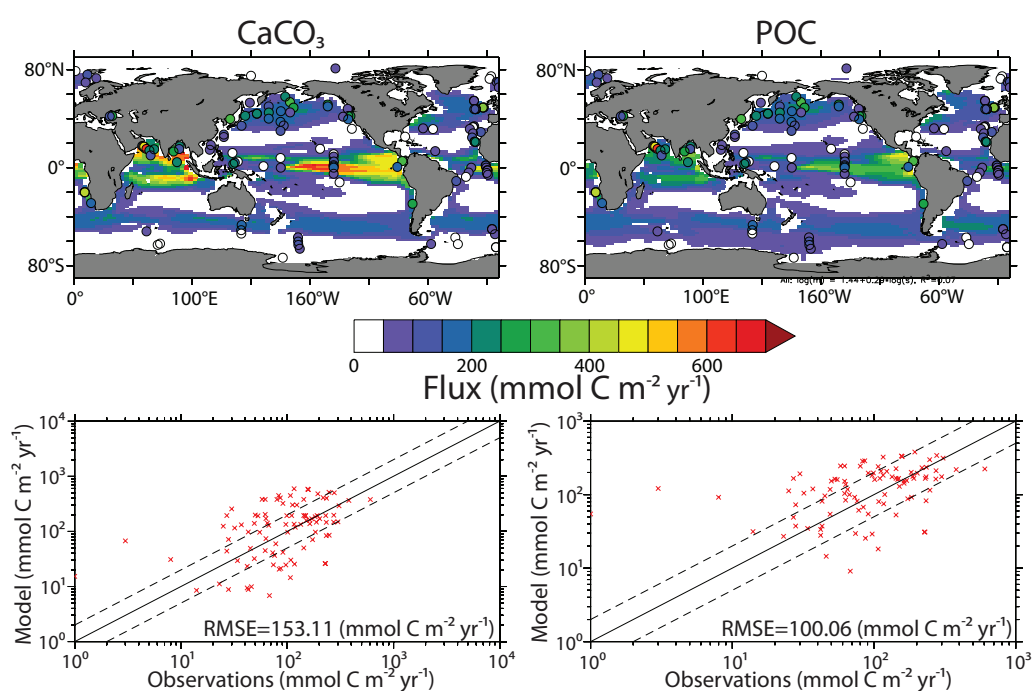


Figure 4.5: OMEGA model average CaCO_3 (upper left) and POC (upper right) export at 2 kilometers depth overlaid by trap data from Honjo et al. (2008). Model/observation regression in bottom panels. Comparable to Figure 3.11.

to be more diverse and more productive under elevated $p\text{CO}_2$ (Sperling et al., 2013). Regardless of the actual mechanism, whether calcifiers become more susceptible or microbes more aggressive with decreasing Ω , application of the scaling factor to microbial fast recycling is perhaps the best physically justified option.

It is possible these results could be achieved using a different parameterisation that likewise favours calcifiers in moderate Ω regions but discourages them in low and high Ω regions. Of the available options, however, none offer this result. Calcifier PFT growth rate is already fairly well constrained as lower than a mixed phytoplankton PFT (Le Quéré et al., 2005), and scaling this rate from one lower value to another lower value would only affect calcifier competitive advantage, not offer a feedback limiting calcifier growth in high Ω regions. The same is also true for scaling of grazing preferences, which can only affect regions where both PFTs are present. Scaling the linear mortality coefficient might improve moderate Ω regions but would not reduce biomass from high Ω regions as overall mortality would be lower there and hence nutrient concentrations would be either unchanged or increased by microbial recycling. It is also important to remember that the UVic ESCM biogeochemistry is a relatively simple model, and spatial distribution of calcifiers might be improved without the application of the scaling factor (see Conclusions in Chapter 3). For example, a prognostic iron cycle or increased competition from additional PFTs might also improve biogeography. Additional PFTs that would compete directly with the calcifier PFT could be the most desirable since they would reduce the over-representation of calcifiers in the model (remember, currently the calcifier PFT represents both calcifying and non-calcifying phytoplankton that share physiological traits).

Chapter 5

UVic ESCM Transient Future Simulations

Anthropogenic carbon dioxide emissions to the atmosphere are altering ocean physics, ecology, and chemistry. This chapter presents an overview of the UVic ESCM ocean biogeochemical response to business-as-usual Representative Concentration Pathway forcing (RCP8.5) with and without an explicit calcifier phytoplankton class and calcite ballast model. All models share a common response, including a transition between two globally dominating feedbacks. The first feedback is a physically driven one that dominates at lower changes in sea surface temperatures (SSTs), where reductions in PO_4^{3-} resupply from the deep ocean causes mixed phytoplankton populations to decline in the low and middle latitudes, and warming and reduction of sea ice cause mixed phytoplankton populations to increase in the high latitudes. Inclusion of calcifiers changes the sign of the global net primary production (NPP) trend from negative to slightly positive over the 21st century as calcifiers replace mixed phytoplankton populations in the middle and low latitudes. Global carbon export production (EP) changes very little. An increase in calcifiers in the middle and low latitudes prevents the advection of excess PO_4^{3-} to the Southern Ocean and has follow-on consequences for the Southern Ocean carbon sink, global denitrification rates, and NO_3^- concentrations. All models demonstrate decline in global mean oxygen concentration though the sign of the change in suboxic water volume depends on whether ballasting is included (decrease) or excluded (increase). The second feedback dominates the first at higher SST changes and is biologically driven. Stratification is reduced and warming-enhanced remineralisation rates rapidly recycle nutrients in the near-surface. This feedback increases global NPP, CaCO_3 EP, and suboxic water volume in all model configurations. The linear relationship be-

tween global NPP change and SST change found by others does not extend beyond a 2–4°C SST change in these simulations. For higher temperature changes, the relationship becomes exponential. The NPP response is greatest when calcifiers are included and the calcite tracer is not. EP trends likewise become positive for higher SST changes, though deep ocean carbon fluxes decline throughout the timeseries for all model configurations (1800–2400). The deep ocean carbon export and oxygen response is found to be highly sensitive to the inclusion of a prognostic calcite tracer for higher SST changes because ballasted detritus is quickly removed from the near-surface remineralisation zone. Calcification and calcite export trends follow those of NPP.

5.1 Methods

The new calcification submodel described in Chapter 3 was implemented in an early UVic ESCM model version 2.9 that did not yet have the capability to simulate RCP scenarios. This ability was introduced in the second level of updates to 2.9, which also includes some changes to the carbon cycle. The model had to be re-tuned and re-equilibrated with the new updates before conducting future simulations. The only parameter that changed between Chapter 3 and Chapter 5 is the linear increase in sinking speed for CaCO_3 in Equation 3.8, which increases from $5.0e^{-2}$ to $6.0e^{-2}$ per second. It might well be that increasing this parameter value in the earlier model version would have likewise improved model performance. Model performance with respect to nutrients and carbon are essentially unchanged.

Four model configurations are included in this chapter. The Keller et al. (2012) model (NOCAL) and calcifier model (CAL) that are compared and described in Chapter 3, an intermediary model that includes the calcifier PFT but not the prognostic calcite tracer (NOCACO3), and the calcifier model that includes an Ω dependency on microbial fast recycling described in Chapter 4 (OMEGA). All models were first integrated for ten thousand years in fully coupled mode (ocean, atmosphere, geosphere, cryosphere, biosphere) using a constant pre-industrial CO_2 atmospheric concentration of 283.8 ppm to establish equilibrium. Equilibration was tested by releasing the constant atmospheric CO_2 concentration forcing and running the models several hundred years to check for stability, while allowing the model to compute atmospheric CO_2 prognostically. Historical CO_2 forcing, as well as historical agricultural, volcanic, sulphate aerosol and CFC emissions and changes to land ice and solar forcing were then applied from year 1800 to 2005 using the PMIP3 (Paleoclimate Modelling Intercomparison Project Phase 3) data compilation (Machida et al.,

1995; Battle et al., 1996; Etheridge et al., 1996, 1998; Flückiger et al., 1999, 2004; Ferretti et al., 2005; Meure et al., 2006). From year 2005 to 2400 the models were forced using increasing CO₂ concentrations and radiative forcing from all non-CO₂ greenhouse gases, fractions of the land surface devoted to agricultural uses, and the direct effect of sulphate aerosols as an alteration of the surface albedo following “business-as-usual” RCP scenario 8.5 (RCP8.5, Riahi et al., 2007). The models diagnose global CO₂ emissions for the prescribed concentration pathway. The physical response (i.e., changes in temperature, salinity, ocean circulation, sea ice) is the same across all model configurations. Differences in model response to climate forcing therefore demonstrate the effect of biogeochemical model structure, such as presence or absence of calcifiers (compare NOCAL to NOCACO₃), instant CaCO₃ dissolution and sinking versus full carbonate tracer (compare NOCACO₃ to CAL), and neutral versus negative calcifier response to ocean acidification (compare CAL to OMEGA).

5.2 Results and Discussion

5.2.1 Changes in Net Primary Production and Biology

Globally integrated net primary production is a key indicator of model performance. In the NOCAL model, global NPP declines until about 2125 and then starts to increase (black line of panel A in Figure 5.1). Decreasing NPP is caused by the global decline of surface nutrients PO₄³⁻ and NO₃⁻ (black lines of panels C and D in Figure 5.1) that reduce the mixed phytoplankton population. Declining surface nutrients are due to the increased stratification of the low and middle latitudes (see changes in ventilation and mixed layer depth, and change in NPP, mixed phytoplankton and surface PO₄³⁻ for NOCAL in Figure 5.2, as well as declines in NPP in the tropics and middle latitudes in panels A of both Figures 5.3 and 5.4, and declines in near-surface nutrients in panels C and D of Figure 5.3) that cut off nutrient resupply from the deep ocean (see increasing PO₄³⁻ concentration below the thermocline in panel E of Figure 5.1). Diazotroph populations expand in parts of the tropics and middle latitude gyres (Figure 5.2) because of their relatively better tolerance of low nutrient concentrations than mixed phytoplankton, but their population size is too small to influence the global NPP trend and overall their productivity declines in the first part of the run (see nitrogen fixation, panel G in Figure 5.1). Historical and 21st century declines in global NPP are consistent with other coupled multi-PFT biogeochemistry-climate models (e.g., Bopp et al., 2013;

Moore et al., 2013a; Steinacher et al., 2010; Yool et al., 2013). They depart from results using an older version of the UVic ESCM (Schmittner et al., 2008) which had used lower phytoplankton growth rates and temperature-independent zooplankton grazing to simulate increases in global NPP throughout a historical and 21st century simulation. These earlier results had identified the UVic ESCM NPP response to increasing temperatures as anomalous, but these new results are in agreement with other published transient simulations to 2100. In the NOCAL simulation, global NPP decreases by 9% by 2100 relative to the pre-industrial equilibrium value owing to declining surface nutrients. Steinacher et al. (2010) found a decrease between 2 and 20% by 2100 using the SRES A2 emission scenario applied to four different climate models for the same reason (decline in nutrient availability). A more recent model survey found a decrease of $8.6 \pm 7.9\%$ from the 1990s to the 2090s, also for the same reason, using RCP8.5 to force ten coupled biogeochemistry models (Bopp et al., 2013). None of the model studies mentioned report simulations beyond 2100 except Schmittner et al. (2008), and also none report a reversal of the NPP trend in the 2100-2400 time range.

The reversal of the global NPP trend in NOCAL occurs as a result of ocean warming, which increases the temperature-dependent biological processes of primary production, detrital remineralisation and phytoplankton fast recycling, as well as from an increase in ocean ventilation and reduction of stratification after 2100 (see changes in ventilation and mixed layer depth, and change in NPP and surface PO_4^{3-} in Figure 5.2). A similar long-term increase in NPP driven by temperature-dependent remineralisation and recovery of near-surface stratification (and, to a lesser extent, warming-enhanced photosynthesis) has been simulated by Schmittner et al. (2008). Fast recycling rates of mixed phytoplankton never decline in spite of the overall decline in NPP and detritus production in the first half of the run (panel B in Figure 5.1), and their increase drives the recovery in global near-surface PO_4^{3-} concentrations in the second half of the run (panel C, Figure 5.1). These processes do not increase uniformly; the largest NPP response occurs in the high latitudes in NOCAL and overrides low and middle latitude NPP declines to dominate the global trend (NOCAL NPP panel in Figure 5.2). Southern Ocean NPP quadruples over the NOCAL run (panel A in Figure 5.5), whereas tropical (between 20°N and 20°S) NPP only just recovers to year 1800 values by 2400 (panel A in Figure 5.3) and NPP in a middle latitude band between 40°S and 60°S never recovers to year 1800 levels (panel A of Figure 5.4). A positive feedback establishes through nutrient transport between the low and middle latitudes and the Southern Ocean, which increases Southern Ocean NPP and reduces low and middle latitude NPP (Figure

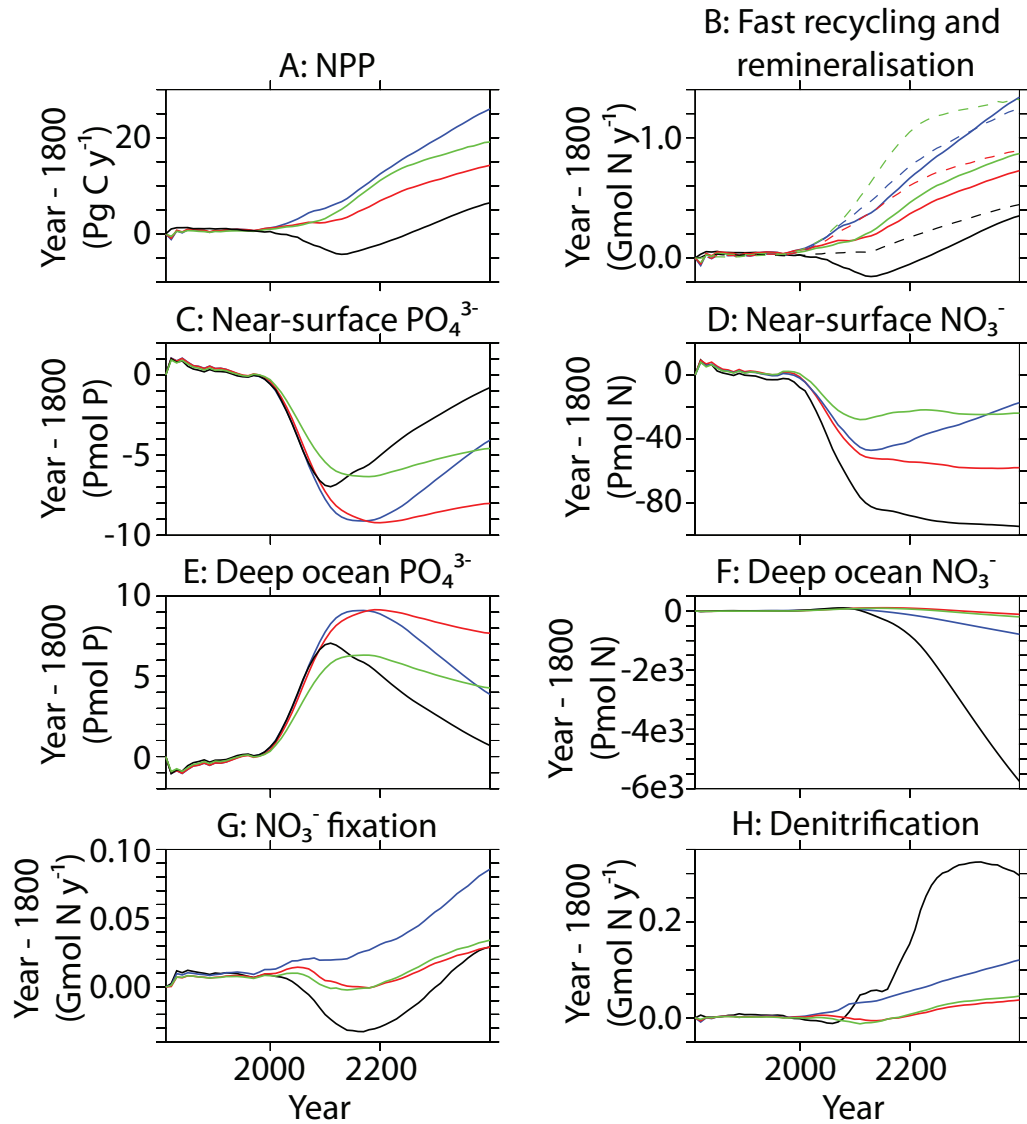


Figure 5.1: Globally integrated change (Year-1800) for NPP (panel A), phytoplankton fast recycling (dashed lines) and detrital remineralisation (solid lines) rates (panel B), PO_4^{3-} and NO_3^- concentration integrated over 0-200 m depth (panels C and D), PO_4^{3-} and NO_3^- concentration below 200 m depth (panels E and F), nitrogen fixation rates (panel G), and denitrification (panel H). Model runs are NOCAL (black line), NOCACO3 (blue line), CAL (red line), and OMEGA (green line).

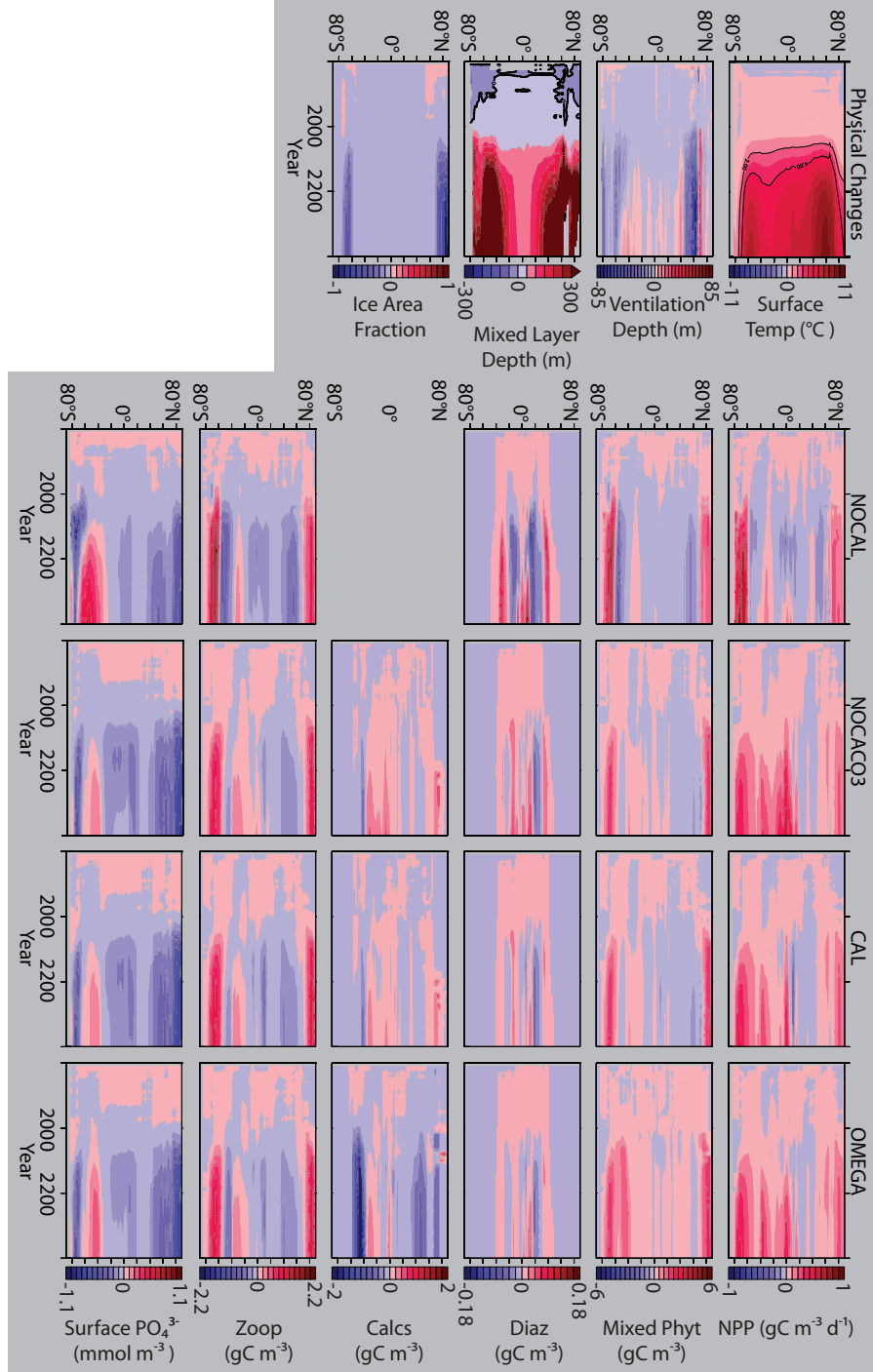


Figure 5.2: Hovmöller diagrams of variable anomalies (Year - 1800) for UVic ESCM model configurations. Mixed layer depth is calculated from a threshold density following Montegut et al. (2004).

5.6). Declining NPP in the tropics and southern hemispheric middle latitudes increases the advection of un-utilised PO_4^{3-} southward. Panels A and B in Figure 5.4 reveal declining NPP in the 40–60°S latitudinal band over the first half of the run is accompanied by transport of PO_4^{3-} across the 40°S latitude that steadily increases from slightly negative (northward) to positive (southward). The excess PO_4^{3-} moves across 60°S into the Southern Ocean and combines with warming sea surface temperatures (SSTs) and reduced sea ice cover to increase NPP, phytoplankton fast recycling and detrital remineralisation (panels A and B of Figure 5.5). Surface PO_4^{3-} declines and deep ocean PO_4^{3-} increases (panels C and E in Figure 5.5) with increases in detrital export. Increasing remineralisation and recycling lowers the Southern Ocean deep ocean oxygen content and increases denitrification (panel G of Figure 5.5, and Figure 5.6). Establishing significant denitrification in the Southern Ocean has follow-on consequences for the global ocean as severely NO_3^- -depleted water (panel F in Figure 5.5) is transported northward and resurfaces in upwelling zones. Large declines in global NO_3^- can be seen in the global means of the near-surface and the deep ocean (panels D and F in Figure 5.1) and are representative mainly of the extra-tropics for near-surface values. Low NO_3^- surface concentrations appearing in the middle latitudes further limits NPP in these regions and increases the transport of excess PO_4^{3-} into the Southern Ocean (Figure 5.4), enhancing the feedback. It is important to note that although near-surface NO_3^- concentrations also decline in the Southern Ocean, they do not reach limiting concentrations and therefore do not impact NPP (Figure 5.5).

There are two distinct regional mechanisms forcing the global NPP trend in NO-CAL that have been described previously (e.g., Bopp et al., 2001; Schmittner et al., 2008; Steinacher et al., 2010; Bopp et al., 2013; Yool et al., 2013; Segschneider and Bendtsen, 2013). Latitudes greater than 60° experience almost no decline in NPP over the simulation as warmer temperatures, increasing nutrients, and decreasing sea ice continuously expand phytoplankton poleward (Figure 5.2). NPP increases substantially on the Atlantic side of the Arctic Ocean, a trend that agrees with the robust multi-model mean of Bopp et al. (2013), and also increases significantly in the Southern Ocean (see map view of change in NPP in Figure 5.6). The Southern Ocean is a region of disagreeing trends across the Bopp et al. (2013) models, which could be partly due to differences in the strength of the nutrient transport feedback described above. These high latitude increases are overshadowed in the global NPP trend until 2100 by decreases in NPP between 60°N and 60°S, where decreasing surface nutrients reduce mixed phytoplankton populations, particularly in the North Atlantic and tropical Indian Ocean basins, and to a lesser extent in the trop-

ical central western Pacific. Declines in these basins are consistent with the robust multi-model trend found by Bopp et al. (2013). After 2100, the global NPP trend reverses and starts to rise because of the large increase in high latitude NPP, reduction of middle and low latitude stratification, and increasing temperature-dependent biological processes. Increases in NPP in the North Pacific over the simulation can be attributed to increased temperature and ventilation depth in the region, which increases both mixed phytoplankton and diazotroph populations.

The importance of phytoplankton community composition for the low latitude and Southern Ocean nutrient feedback is highlighted in the very different global NPP response of the models that include calcifiers (schematic shown in Figure 5.6). Because calcifiers have a lower nutrient half saturation constant than mixed phytoplankton, decreasing surface nutrient concentrations in the low and middle latitudes in the first half of the model runs increase their relative advantage, and the population increases in the southern Pacific and Atlantic basins (Figure 5.2). Global NPP never declines in NOCACO3, CAL, and OMEGA in spite of globally declining surface nutrients (Figure 5.1) because of the calcifiers replacing mixed phytoplankton. Strong increases in NPP in the 40–60°S latitudinal band for the models with calcifiers compensate for increased southward transport of PO_4^{3-} into the region and result in lower near-surface PO_4^{3-} concentrations and a smaller increase in PO_4^{3-} transport into the Southern Ocean than in NOCAL (Figure 5.4). Less fertilisation of the Southern Ocean in NOCACO3, CAL, and OMEGA results in a lower regional NPP response and strong denitrification fails to develop (Figures 5.5 and 5.6). The absence of significant Southern Ocean denitrification as well as the higher tolerance of calcifiers to nutrient depletion prevents a decrease in NPP in the middle and low latitudes (Figures 5.3 and 5.4), thus maintaining mixed phytoplankton and diazotroph populations in these regions better than in NOCAL (Figure 5.2). Maintenance of NPP by calcifiers in the low and middle latitudes also has the effect of increasing the global warming-enhanced biological processes, with fast recycling and detrital remineralisation rates rising more quickly in the calcifier models than in NOCAL globally and in the tropics (panels B in Figures 5.1 and 5.3). Eventual large losses of calcifiers in the OMEGA model from acidification-enhanced fast recycling occur after warming-enhanced biological processes dominate the global NPP trend, and the opportunity for a large Southern Ocean nutrient exchange feedback to develop is missed.

Like my calcifier models, Manizza et al. (2010); Marinov et al. (2013); Moore et al. (2013a); Yool et al. (2013) also project a global increase in the proportion of small phytoplankton (calcifiers) over the 21st century, but unlike the UVic ESCM calcifier

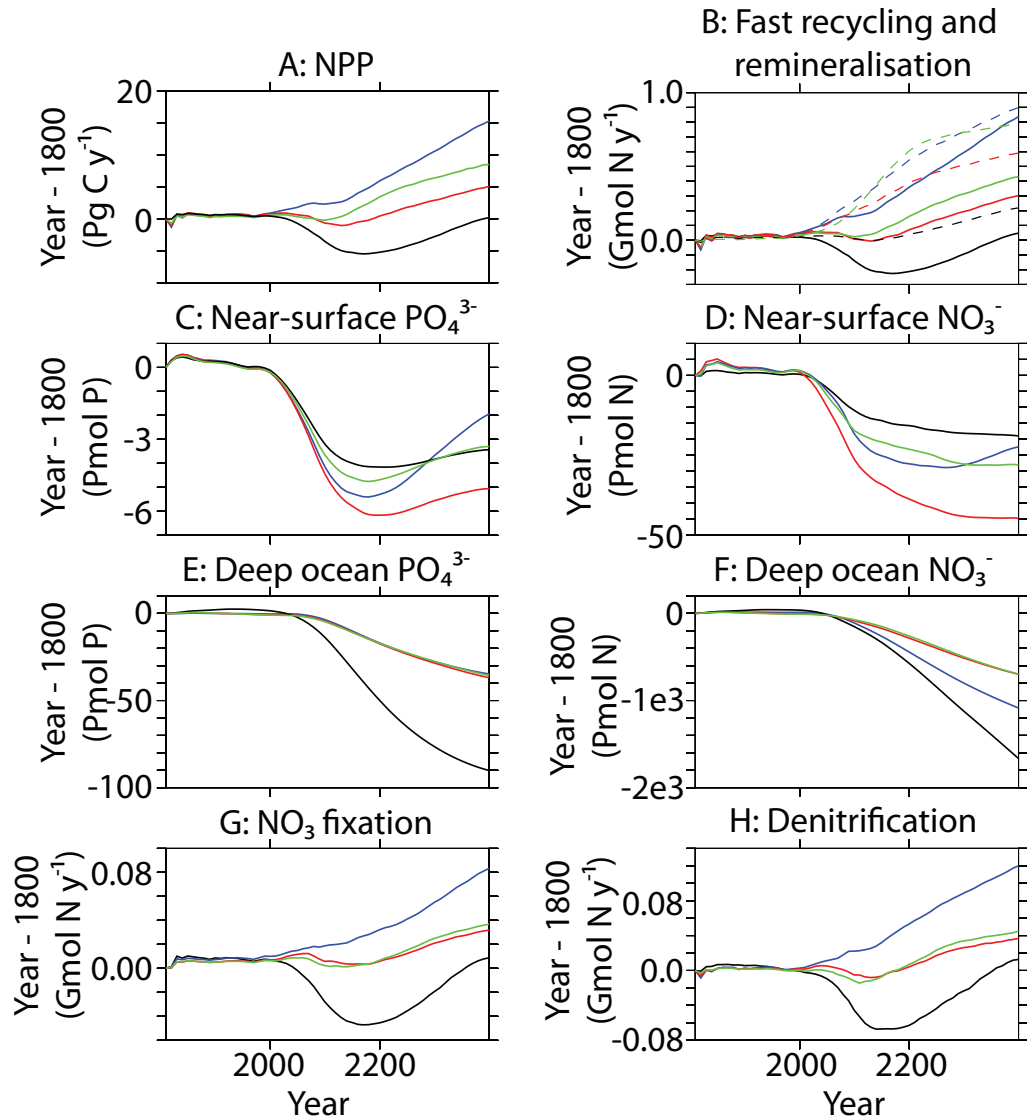


Figure 5.3: Biogeochemical change (Year-1800) integrated over the tropics (20°N to 20°S) for NPP (panel A), phytoplankton fast recycling (dashed lines) and detrital remineralisation (solid lines) rates (panel B), PO_4^{3-} and NO_3^- concentration integrated over 0-200 m depth (panels C and D), PO_4^{3-} and NO_3^- concentration below 200 m depth (panels E and F), nitrogen fixation rates (panel G), and denitrification (panel H). Model runs are NOCAL (black line), NOCACO3 (blue line), CAL (red line), and OMEGA (green line).

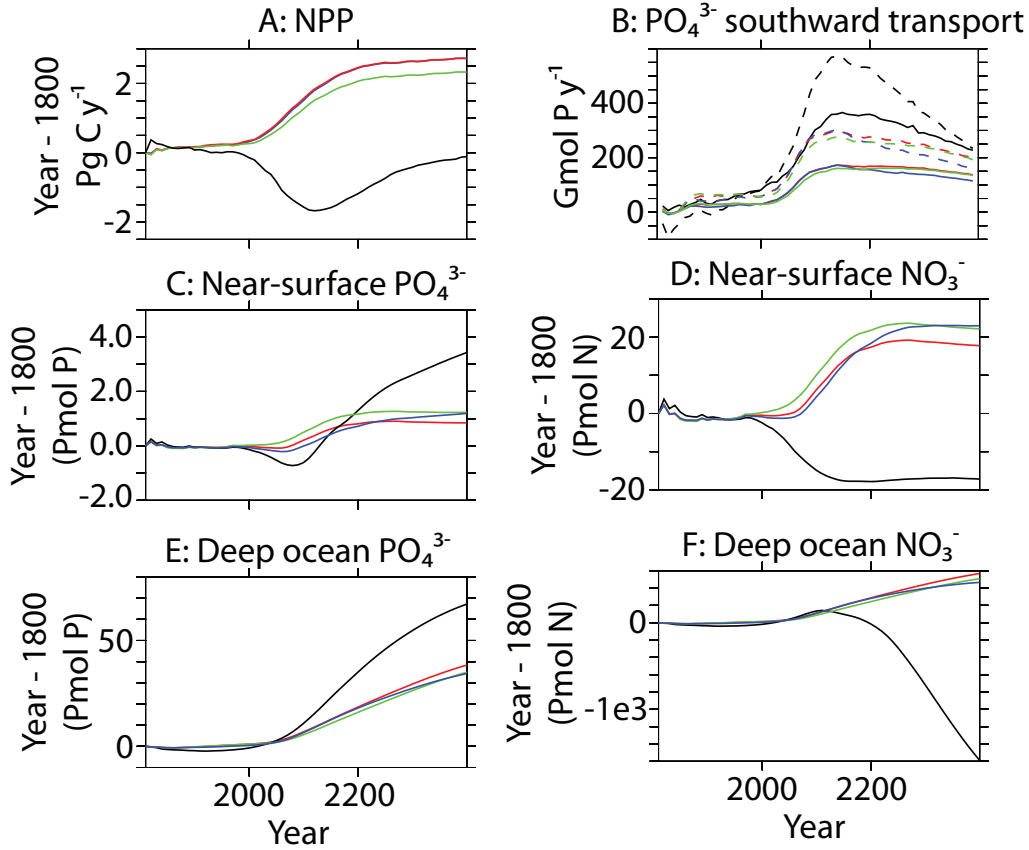


Figure 5.4: Biogeochemical response integrated over Southern Hemisphere high-middle latitudes (40°S to 60°S) for NPP (panel A), PO_4^{3-} southward transport (panel B: dashed lines are across the 40°S latitude, solid lines are across the 60°S latitude), PO_4^{3-} and NO_3^- concentration change integrated over 0-200 m depth (Year-1800, panels C and D), and PO_4^{3-} and NO_3^- concentration change below 200 m depth (Year-1800, panels E and F). Model runs are NOCAL (black line), NOCACO3 (blue line), CAL (red line), and OMEGA (green line). All panels except B show anomalies from 1800.

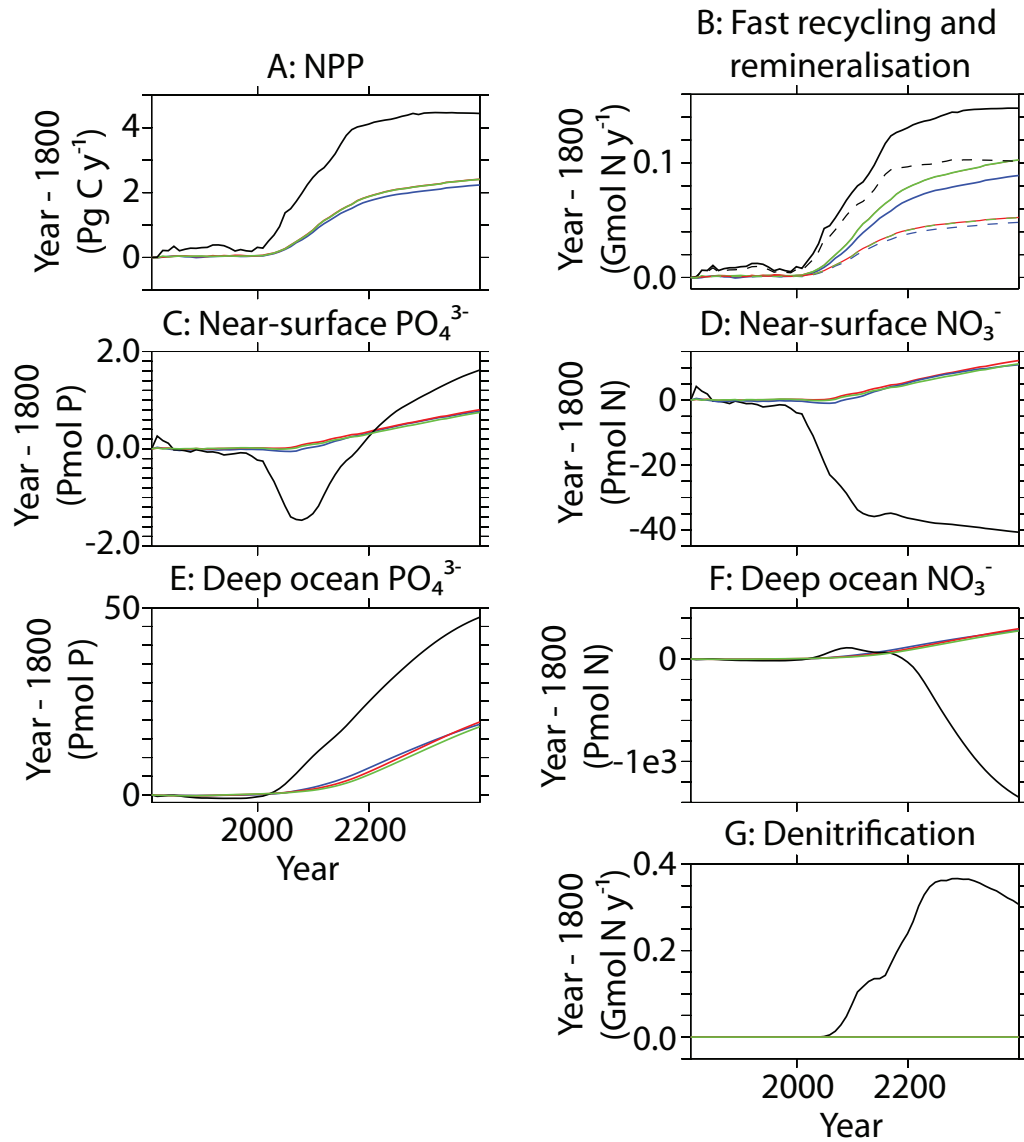


Figure 5.5: Biogeochemical change (Year-1800) integrated over the Southern Ocean (60°S to 90°S) for NPP (panel A), phytoplankton fast recycling (dashed lines) and detrital remineralisation (solid lines) rates (panel B), PO_4^{3-} and NO_3^- concentration integrated over 0-200 m depth (panels C and D), PO_4^{3-} and NO_3^- concentration below 200 m depth (panels E and F), and denitrification (panel G). Model runs are NOCAL (black line), NOCACO3 (blue line), CAL (red line), and OMEGA (green line).

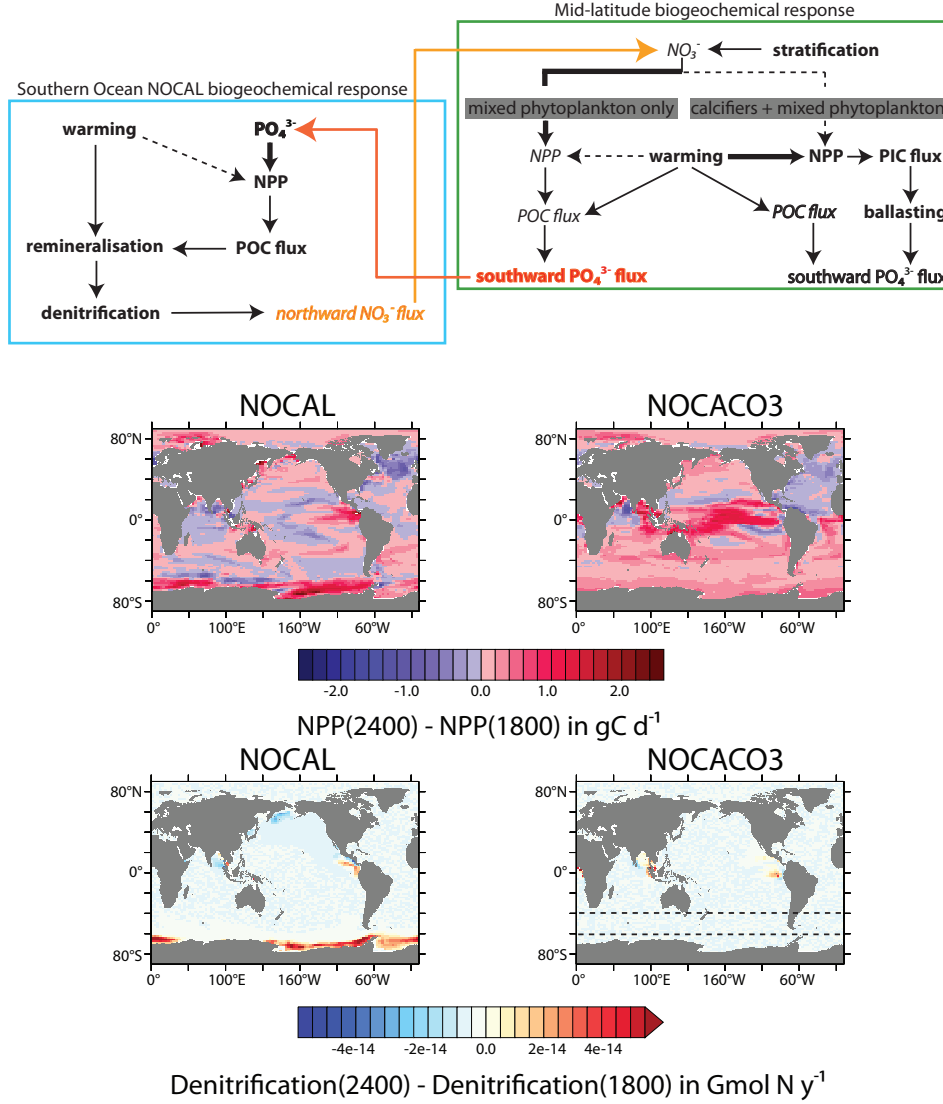


Figure 5.6: Biogeochemical response schematic for the middle latitudes and Southern Ocean (green and blue boxes). Increases with climate change are represented in bold font. Decreases with climate change are represented in italic font. Regular font indicates little or no change with climate forcing. Bold arrows indicate the dominant factor influencing change in NPP. Dashed arrows indicate the secondary factor influencing change in NPP. Nutrient feedback between regions is shown in coloured arrows. Depth-integrated change in NPP (2400-1800), as well as depth-integrated change in denitrification (2400-1800) are also shown for NOCAL and NOCACO3. Dashed lines on the NOCACO3 denitrification plot indicate the 40 and 60°S latitudes. CAL and OMEGA model NPP and denitrification change are similar to that of NOCACO3.

models global NPP still declines in their models. Biological community composition is already recognised as critical to determination of the overall trend in NPP (e.g., Marinov et al., 2013). NOCACO3, CAL, and OMEGA have overestimated calcifier contribution to total biomass (Kvale et al., 2014, and Chapter 3), which likely overestimates the global NPP contribution of calcifiers in both pre-industrial and future scenarios. Lower contributions by calcifiers to NPP in the low and middle latitudes could allow for a global decline in NPP and a larger nutrient feedback between these regions and the Southern Ocean. It is also possible that the omission of an explicit diatom PFT (which is particularly susceptible to stratification and inhabits the high latitudes; see Marinov et al. 2010; Moore et al. 2013a; Yool et al. 2013) could alter the Southern Ocean response.

Choice of parameterisation of particle export and remineralisation by model PFTs can also control surface nutrient resupply and resultant NPP trends (e.g., Taucher and Oschlies, 2011; Segschneider and Bendtsen, 2013). For instance, low latitude increases in implicit calcifiers in Moore et al. (2013a) were not able to offset declines in global NPP driven by the other PFTs because of differences in the export efficiency across the PFTs. In the NOCACO3 model there are no differences between calcifier and mixed phytoplankton PFT carbon export efficiency, and thus calcifier replacement of mixed phytoplankton serves as an equivalent substitution. In CAL and OMEGA, however, calcifiers (including zooplankton) are more efficient exporters because of their ability to ballast detritus in protective CaCO_3 . Increased global carbon and nutrient export efficiency as phytoplankton calcifiers take over should theoretically reduce global NPP, but these runs show the relevance of calcifier biogeography, as regions where calcifiers expand are also the regions where warming-enhanced biological processes increase the earliest. The effect of increasing carbon and nutrient export efficiency in CAL and OMEGA instead reduces the rate of increase in global and tropical NPP and the rate of global and tropical detrital remineralisation relative to that of NOCACO3, and decreases the near-surface and deep ocean nutrient response in the second half of the runs (compare red and green lines to blue lines in Figures 5.1 and 5.3 panels). Tropical and global NO_3^- fixation and denitrification trends are also sensitive to the ballast models in CAL and OMEGA. Less denitrification develops in the low latitudes in CAL and OMEGA relative to the NOCACO3 simulation because CaCO_3 ballasting of POC reduces remineralisation rates, which reduces oxygen consumption. Less NO_3^- fixation occurs because lower remineralisation rates keep absolute surface PO_4^{3-} concentrations lower in the CAL and OMEGA models (not shown), which limits all phytoplankton populations including the diazotrophs. Model responses in global carbon export are

described further in a later section.

5.2.2 NPP/SST Sensitivity

The trend reversal of global mean NPP in NOCAL in spite of continuously increasing global mean SSTs suggests a more complex relationship between these two quantities in the UVic ESCM than the linear one previously shown by Bopp et al. (2013) and Moore et al. (2013a). Figure 5.7 illustrates the different relationships between changes in NPP and SSTs for all model configurations. All models show a transition between two globally dominating feedbacks. In NOCAL, the relationship between % change in NPP and change in SST is negative and quasi-linear only until about 4°C of warming, whereupon the relationship becomes positive and exponential. At SST changes under about 4°C in NOCAL, reduced nutrient supply for phytoplankton dominates the global NPP trend (a physically-driven feedback), but a tipping point is reached at about 4°C whereupon nutrients are no longer globally limiting because of warming-enhanced biological processes (a biologically-driven feedback) and a global reduction of stratification (Schmittner et al., 2008). An exponential relationship between NPP and SSTs beyond 4°C of change is not altogether surprising since phytoplankton growth, zooplankton grazing, phytoplankton fast recycling, and POC remineralisation rates are all exponentially temperature dependent in the UVic ESCM. It is possible other models using temperature dependent rates might achieve a similar sign reversal in the NPP/SST relationship; neither Bopp et al. (2013) nor Moore et al. (2013a) plot the relationship past a 4°C SST change, nor integrate experiments past 2100.

The inclusion of calcifiers in the NOCACO3 model alters the NPP/SST relationship from one that is negative and linear and becomes positive and exponential at about 4°C of change for NOCAL, to one that is positive and linear and becomes positive and exponential at about 2°C of change. The NOCACO3 model transitions to a warming-enhanced biological process-dominated feedback earlier than NOCAL because of increased NPP in the low latitudes throughout the simulation, which is the region dominated earliest by warming-enhanced fast recycling and remineralisation.

The addition of a prognostic calcite tracer reduces model NPP sensitivity to SST warming relative to the NOCACO3 configuration. In the CAL configuration trends in all plotted variables share the same temporal and spatial patterns, but not the magnitude, with the NOCACO3 configuration. This is because of the added effect of calcite-ballasted detritus, which increases over the simulation alongside the calcifier population and effectively removes nutrients from the surface and from the

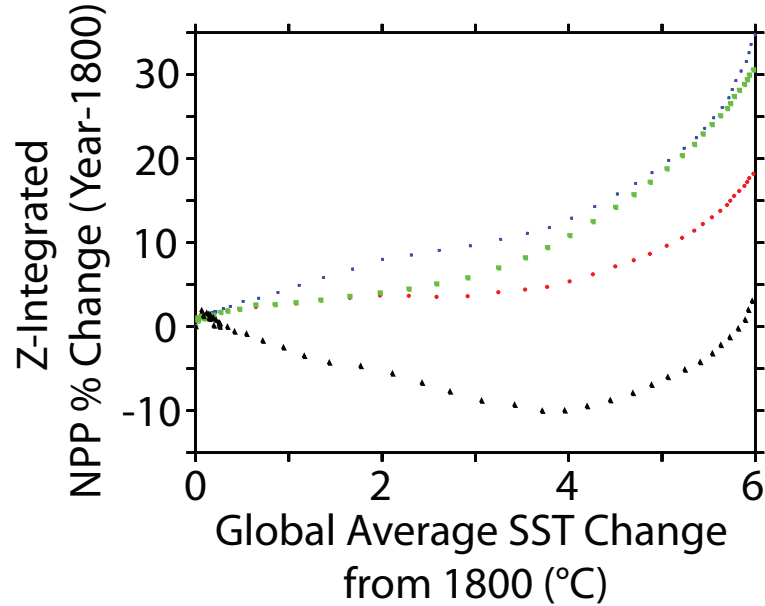


Figure 5.7: Global depth-integrated percent change in NPP (Year-1800) versus global average SST change (Year-1800) for NOCAL (black), NOCACO₃ (blue), CAL (red), and OMEGA (green).

zone of warming-enhanced remineralisation (thereby mitigating the remineralisation feedback). Eventually, however, even the mitigating effect of ballasting cannot override the effect of warming-enhanced remineralisation, and the NPP/SST relationship becomes exponential.

Declining saturation state increases the microbial recycling rates of phytoplankton calcifiers in the OMEGA middle and low latitudes, and increases the sensitivity of the NPP/SST relationship relative to the CAL model. The increased sensitivity of model calcifiers in OMEGA to enhanced remineralisation causes the global NPP trend to depart from that of CAL just after 2100, or just after 2°C of SST warming, whereupon the trend becomes strongly positive and exponential. Above a 5°C change in SST, the NPP trend more closely follows that of NOCACO₃, which indicates a severely reduced mitigating ballasting effect.

5.2.3 Changes in Carbon Export

Eventual increases in global NPP relative to pre-industrial values in NOCAL do not carry through to carbon export away from the surface (Figure 5.8). Global CaCO₃ and POC export from the near-surface decline alongside global NPP over

the historical period and 21st century in the NOCAL configuration, but while NPP and CaCO_3 flux eventually increase beyond the pre-industrial level, POC export production (EP) does not, and deep water POC flux declines continuously over the simulation. The decline in POC flux in NOCAL is partly due to the decline of NPP in the middle and low latitudes, but mostly due to the warming-enhanced detrital remineralisation rate in the near-surface, which removes POC from export even as NPP and CaCO_3 export increase.

In the NOCACO3 simulation, replacement of mixed phytoplankton by low and middle latitude calcifiers results in a more modest decline in globally integrated POC EP to 2100, but a much larger sensitivity to increasing temperature-dependent remineralisation rates and a resulting larger decline in deep ocean POC flux by 2400 (Figure 5.8). CaCO_3 flux, on the other hand, increases the most of all the runs because of the large NPP/SST sensitivity.

The moderating effect of the ballast model is apparent in the CAL results, which shows the smallest total long-term decline in global deep ocean POC flux and the smallest CaCO_3 EP rate increase in the remineralisation-dominated ocean (Figure 5.8). Increasing globally integrated CaCO_3 EP over the NOCACO3 and CAL simulations as a response to increasing NPP agrees with Schmittner et al. (2008), and is not reproduced in models that project declining NPP (e.g., Moore et al., 2013a; Yool et al., 2013).

OMEGA model POC EP trends at 130 meters depth follow those of CAL because even though ballasting by calcifiers is reduced and eventually eliminated by decreasing Ω values, ballasting by zooplankton-derived CaCO_3 increases under warming-enhanced remineralisation as increasing NPP increases their food supply. Zooplankton-derived CaCO_3 therefore becomes increasingly important for global export trends as calcifier-derived CaCO_3 production is decreased and dissolution is increased by increasing ocean acidification, but zooplankton CaCO_3 production is not affected.

The addition of calcifiers to the model in the NOCACO3, CAL, and OMEGA configurations decreases the early POC EP response (near-surface POC fluxes are reduced less in these models over the first part of the runs) by maintaining NPP in the warmest and lowest nutrient regions. The application of a CaCO_3 tracer mitigates the longer-term response because explicit CaCO_3 ballasting protects some POC from remineralisation, so near-surface POC fluxes do not increase, and deep ocean POC fluxes do not decline, as much in the CAL and OMEGA models as in the NOCACO3 model. In contrast, addition of calcifiers (but no ballasting) to the PISCES-T model further reduced global EP and ocean carbon uptake relative to the

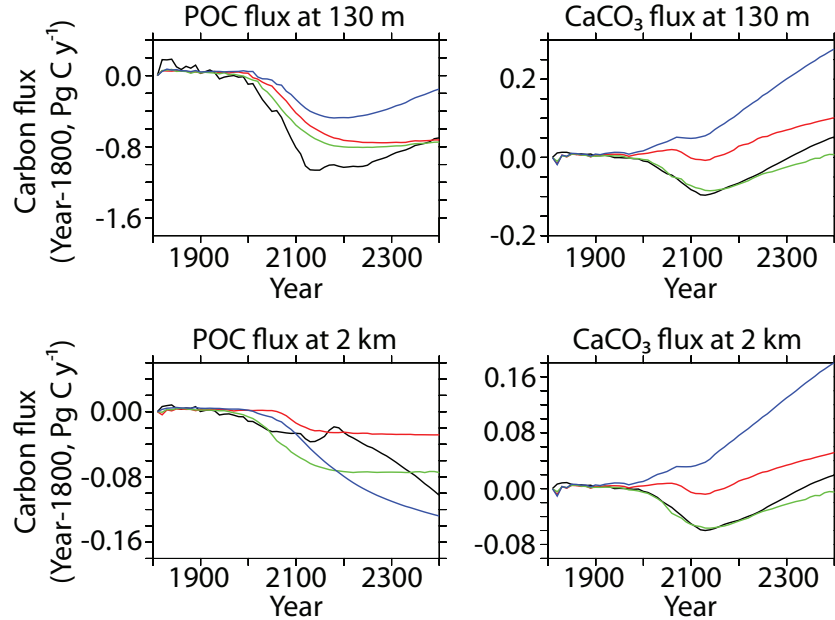


Figure 5.8: Timeseries of export production for NOCAL (black line), NOCACO3 (blue line), CAL (red line), and OMEGA (green line) at 130 meters depth (top row) and 2 km depth (bottom row). Left panels are POC, right panels are CaCO_3 .

control experiment in Manizza et al. (2010) because expansion of calcifiers reduced the zooplankton population (who prefer silicifiers in their model), which reduced carbon EP and export efficiency more than if no calcifiers were included in the model. This zooplankton response is not seen in CAL because zooplankton grazing is not preferential between calcifiers and mixed phytoplankton, and reinforces the conclusion that ecosystem model parameterisation choice critically determines model EP and export efficiency behaviour in climate transitions (Taucher and Oeschles, 2011; Segschneider and Bendtsen, 2013).

Increases in high latitude POC EP caused by expanding phytoplankton populations, offset by the decline of near-surface POC EP everywhere else is a robust multi-model result described in Bopp et al. (2013). This trend occurs in all of my model configurations in the near-surface, but only extends to the deep ocean in NOCAL (not shown). It is noteworthy that alteration of the global carbon export pathway by the addition of a calcifier PFT in NOCACO3, CAL, and OMEGA results in large Southern Ocean trend differences across model configurations not only for NPP but also for POC fluxes. This is an interesting result given the calcifier PFT is never dominant in this region.

5.2.4 Changes in Oxygen

Model declines in simulated global oxygen content over the 21st century (Table 5.1) are generally in agreement with the Bopp et al. (2013) estimate of $3.45 \pm 0.44\%$, though the NOCAL model simulates a substantially larger decline of 5.0% due to the increase in detrital remineralisation in the Southern Ocean over this time period. Percentage differences in total oxygen loss across model configurations are reduced over the simulations as microbial processes begin to dominate, with only a 0.9% trend difference between end members by 2400.

Expansion of suboxic zones (following Oschlies et al. 2008, regions where oxygen concentrations are less than or equal to 5 mmol m^{-3}) show greater sensitivity to model configuration (Figure 5.9 and Table 5.1). In the models that do not include ballasting (NOCAL and NOCACO3), by 2100 suboxic volume has increased 2.3 and 14.2%, respectively, relative to the volume at 1800. Expansion of the suboxic regions occurs because of increased respiration rates and decreased solubility in both models as well as increased biological activity in the Southern Ocean in NOCAL. These estimates agree somewhat with Yool et al. (2013), who found a suboxic volume increase of 12.5% for the 2090s relative to the 1990s using RCP8.5, and are much lower than Oschlies et al. (2008), who found a 50% increase by the end of the century using the A2 SRES scenario and a variable C:N remineralisation ratio. The much larger suboxic volume increase in NOCACO3 than in NOCAL is a result of the higher NPP/SST sensitivity of the calcifier models. In the models that include ballasting (CAL and OMEGA), suboxic volume declines by 14.8 and 26.1%, respectively, by 2100. Thermodynamic solubility still decreases, and respiration rates still increase in these models (though not as quickly in the OMEGA model since calcifiers have a lower microbial recycling rate in carbonate saturated water). These trends decrease the total oxygen content, but the suboxic volume is affected by expansion of the calcifiers, which locally increase CaCO_3 export in the Eastern Equatorial Pacific, removing detritus from microbial degradation and contracting the suboxic zone. The relative impact of ballasting on oxygen trends increases as warming-enhanced remineralisation and fast recycling becomes more dominant. By 2400 the CAL and OMEGA models suboxic volume has expanded by only 2.8 and 8.2%, respectively, while in the NOCACO3 and NOCAL models the volume has increased by 60.9 and 724.9%, respectively. The exceptional expansion of suboxic volume in the NOCAL model occurs in the Southern Ocean and accompanies the large regional increase in NPP. Hofmann and Schellnhuber (2009) identified the weakening of the ballast export pathway under ocean acidification as a substantial driver of the expansion of

Table 5.1: Globally integrated pre-industrial oxygen content and simulated trends.

Model	1800 O ₂ Content in Pmol	2100 % Content Change	2400 % Content Change	2100 % Suboxic Volume Change	2400 % Suboxic Volume Change
NOCAL	176	-5.0	-14.7	+2.3	+724.9
NOCACO3	279	-3.2	-14.1	+14.2	+60.9
CAL	270	-3.2	-15.0	-14.8	+2.8
OMEGA	266	-3.1	-14.5	-26.1	+8.2

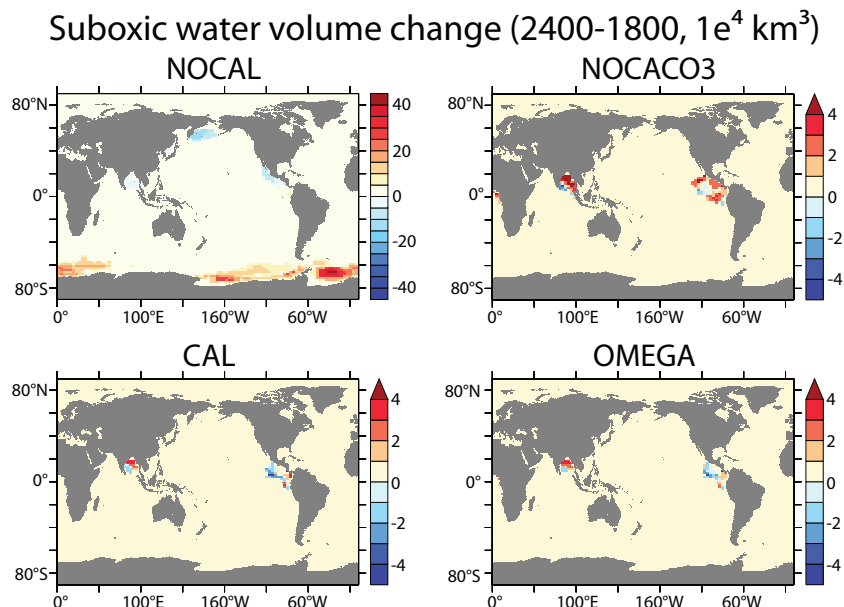


Figure 5.9: Change in suboxic (O_2 less than 5 mmol m^{-3}) water volume between 1800 and 2400 in all model configurations. Note the different scale for NOCAL.

hypoxic zones. These results show that inclusion of ballasting in the UVic ESCM affects the sign of the 21st century change in suboxic water volume (while within the physically-dominated climate feedback), and substantially reduces the long-term simulated expansion of suboxic water volume (in the biologically-dominated climate feedback). These results also show that the reduced ballasting pathway in OMEGA compared to CAL roughly doubles the suboxic trend. The present generation of climate models show relatively poor agreement both with each other as well as observations with respect to modern and future oxygen trends (Bopp et al., 2013), and this might very well be related to the variable formulations of calcification and carbon export, as well as to the strength of the Southern Ocean nutrient exchange feedback described earlier.

5.2.5 Changes in Carbonate Chemistry and DIC

Chemistry-dependent calcite dissolution in the CAL and OMEGA models result in only minor additional reductions in surface and deep ocean calcite saturation state over the simulations compared to NOCAL and NOCACO3 simulations (not shown). In all model configurations, a stabilisation of surface carbonate chemistry occurs shortly after 2200 that corresponds with stabilisation of atmospheric CO_2 concen-

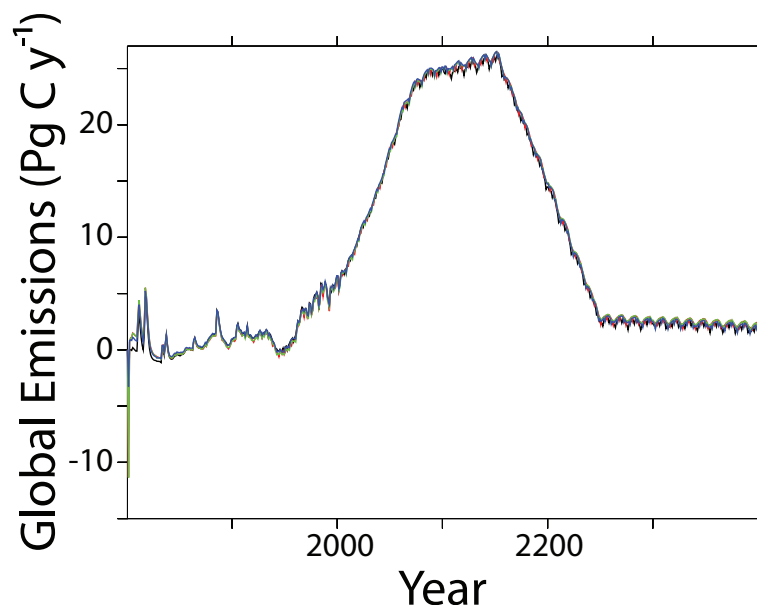


Figure 5.10: Diagnosed global carbon emissions for NOCAL (black line), NOCACO3 (blue line), CAL (red line), and OMEGA (green line).

trations. The first year calcite and aragonite undersaturation is reached in surface waters for all model configurations varies by no more than a decade. Differences in diagnosed global accumulated emissions are also small across model configurations (Figure 5.10), with a difference of 111 Pg C in allowable emissions between 1800 and 2400 (5013 Pg C in NOCAL, 5124 Pg C in NOCACO3, 5103 Pg C in CAL, 5101 Pg C in OMEGA).

Depth integrated DIC trends differ across model configurations mostly in the Southern Ocean (Figure 5.11), where the much larger increase in NPP in the NOCAL simulation results in a larger quantity of DIC in this region. These results reinforce the conclusion of Manizza et al. (2010) and Bopp et al. (2013) that the Southern Ocean is particularly sensitive to ecosystem model parameterisation, and that ocean carbon uptake increases with increasing EP (Manizza et al., 2010).

5.3 Summary and Conclusions

The experiment described in this chapter highlights the importance of biogeochemical model parameterisation in determining the transient behaviour of the ocean carbon cycle during climate transitions. Though each model (NOCAL, NOCACO3, CAL, and OMEGA) has very similar equilibrium states, which are described in pre-

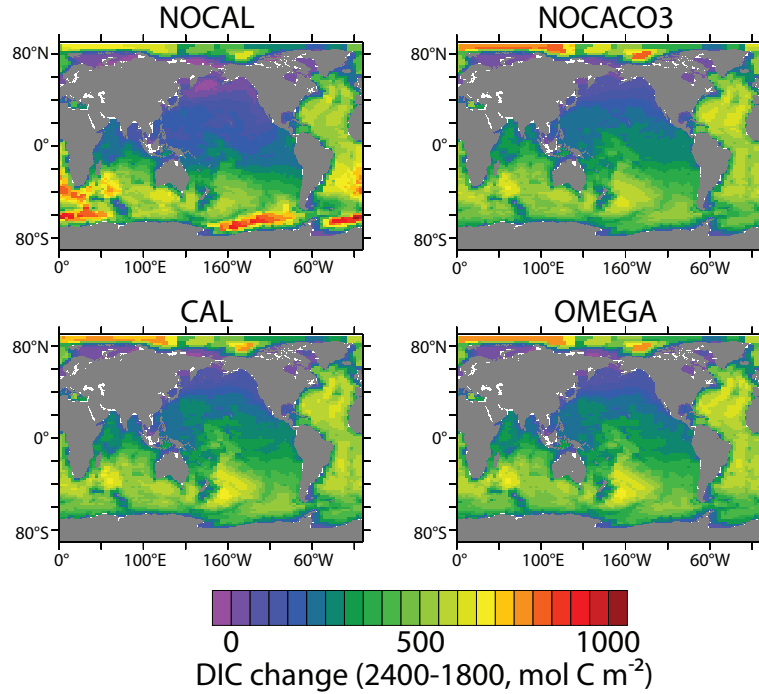


Figure 5.11: Depth integrated DIC anomalies (2400-1800) for model configurations.

vious chapters, each model's biogeochemical behaviour under forcing is unique both in global and regional trends. Overall, however, the models share a common response of a transition between two dominant feedbacks. The first is a physically-driven one that dominates at lower changes in sea surface temperatures, where reductions in PO_4^{3-} resupply from the deep ocean causes mixed phytoplankton populations to decline in the low and middle latitudes. Increased warming and reduced sea ice cover increases the mixed phytoplankton population in the high latitudes. In the NOCAL model, global NPP, POC and CaCO_3 EP decline over the first half of the simulation as a result of the low latitude trend. In the models that contain calcifiers (NO-CACO3, CAL, OMEGA), the higher nutrient affinities of the calcifiers allow them to replace the mixed phytoplankton population in the stratifying low latitudes, and global NPP, POC and CaCO_3 EP change less.

The replacement of mixed phytoplankton by calcifiers in the low and middle latitudes has a strong follow-on effect for the Southern Ocean, which fails to develop as a large carbon sink in the calcifier models. This is because maintenance of NPP in the low and middle latitudes prevents the advection of excess PO_4^{3-} into the Southern Ocean. In the NOCAL model, this excess PO_4^{3-} increases Southern Ocean NPP and associated detrital remineralisation and denitrification. NO_3^- -depleted water ad-

vects northward and surfaces in upwelling regions, and NPP in the middle latitudes becomes increasingly NO_3^- -limited, resulting in more excess PO_4^{3-} . This Southern Ocean/middle latitude nutrient exchange acts as a positive feedback for increasing Southern Ocean NPP in the NOCAL model, but not in the calcifier models. This nutrient exchange remains a secondary actor with respect to the global NPP NOCAL trend until transition to the second, biologically-driven dominant feedback occurs. It is important to note that the UVic ESCM includes a parameterisation of wind stress anomalies following Weaver et al. (2001), which produces a poleward shift and increase in the strength of the Southern Ocean westerlies in all model configurations (not shown). Real changes in wind patterns will likely differ somewhat from the model and could alter the actual SST and NPP response. That reduction of NPP in one region can potentially increase NPP in another via nutrient advection, with follow-on effects for deep carbon export and oxygen is a result that highlights just how accurately a model must represent phytoplankton physiology, ecological competition (and of course, physics) in order to adequately assess regional biogeochemical consequences to environmental change. Further testing of this Southern Ocean NPP mechanism is warranted given its potential relevance for carbon uptake, denitrification, and oxygen concentration.

The sign of the global NPP trend under the first physically-driven feedback differs between the models that include calcifiers and the model that does not. So how well do these model results reflect reconstructions of the historical period? A recent model-data hindcast simulation by Laufkötter et al. (2013) suggests global NPP and EP declined between 1960 and 2006 on an order similar to that of the NOCAL model. Also like the NOCAL model, their simulation shows the strongest declines occurring in the central-western Pacific (not shown). If a low-latitude/Southern Ocean nutrient exchange feedback is currently forming it is probably still too early to detect according to our results, which agree with the finding of no significant trend in Southern Ocean NPP over the time period by Laufkötter et al. (2013).

Oxygen trends under the first feedback depend on whether CaCO_3 ballasting is resolved, with expanding suboxic zones in the models that do not include it and contracting zones in those that do. This is because increased NPP in the ballast models has a corresponding increase in CaCO_3 flux in the eastern equatorial Pacific suboxic zone, which protects more of the POC flux from remineralisation and raises near-surface oxygen concentrations. The models without ballasting, however, show increased POC flux in this same region which decreases near-surface oxygen concentrations.

The second biologically-driven feedback dominates the first for higher sea surface

temperatures when near-surface stratification weakens and is driven by warming-enhanced remineralisation rates, which compensate for reductions in nutrient resupply by rapidly recycling carbon and nutrients in the near-surface. This feedback increases global NPP, CaCO_3 EP, and suboxic water volume in all model configurations. Transition to this second feedback in all model configurations raises the possibility that trends observed in NPP over recent decades cannot be extrapolated far into the future. POC EP response is dependent on whether the model accounts for detrital ballasting by calcite; the models that contain a ballasting parameterisation (CAL and OMEGA) show a mitigated increase in near-surface POC production, and a mitigated decline in deep ocean POC export because the calcite protects POC from near-surface remineralisation and continues to effectively remove it to the deep ocean throughout the simulations. On the one hand, no CMIP5 model currently accounts for the ballasting effect, which suggests they are not appropriate tools for examining long-term trends in POC export and oxygen. On the other hand, whether a physical ballast mechanism exists beyond a globally-relevant scale has recently been questioned by Wilson et al. (2012). Given the potential importance of ballasting to a transitioning carbon cycle, additional clarification of this issue is needed.

The transition between the two dominating feedbacks depends on model parameterisation. Including calcifiers causes the model to become more sensitive to warming-enhanced remineralisation because the calcifiers maintain NPP in the warmest (low and middle latitude) regions. The transition to the second feedback occurs at lower values of global sea surface temperature change (around 2°C), whereas in the NOCAL model the transition occurs around 4°C sea surface temperature change with NPP response occurring primarily in the Southern Ocean. A 2°C change is a well-established threshold for dangerous climate change (e.g., Graßl et al., 2003), and this analysis adds another reason to support this guardrail. This analysis also suggests that the low to middle latitude NPP response is going to be one of the more important indicators of system sensitivity to observe as ocean change continues, and that accurately reproducing phytoplankton competition in models is of utmost importance for understanding tipping points and dangerous thresholds in the global carbon cycle. Given the impact this feedback has on global NPP, further investigation of temperature-dependent remineralisation in models is warranted.

There are several shortcomings in the models presented here that likely affect the above conclusions. As mentioned in previous chapters, the calcifier models overrepresent the PFT in total biomass and in low latitudes, and underrepresent the PFT in high latitudes. This bias could contribute an over-sensitivity of the calcifier

models to warming-enhanced remineralisation. Replacement of mixed phytoplankton by calcifiers is wholly dependent on shifts in relative competitive advantage, at least some of which is artificial to the model and would change by including more PFTs. Furthermore, while the OMEGA model shows a decline in and eventual cessation of calcification contributions by calcifiers, zooplankton calcification continues. None of the models include globally decreasing net calcification with increasing CO_2 concentration (Riebesell et al., 2000), which would doubtless increase the long-term model sensitivity to warming-enhanced remineralisation, but is also debatable (Lohbeck et al., 2012). Furthermore, using a single dissolution parameterisation for zooplankton and calcifier CaCO_3 ignores the likely significant contribution of aragonite dissolution (Gangstø et al., 2008), which would also increase model sensitivity to warming-enhanced remineralisation and magnify oxygen sensitivity.

Chapter 6

Conclusions

Anthropogenic forcing of the global carbon cycle is affecting and will continue to affect ocean biogeochemistry. This thesis examined parameterisations of the ocean carbon cycle in two climate models, and assessed their simulations of pre-industrial, modern, and hypothetical future climate states. All of the model parameterisations do a reasonable job of simulating observed pre-industrial ocean metrics such as carbon and nutrient distributions and carbon fluxes. Their behaviours under hypothetical future climate forcing, however, depart substantially and are dependent upon model structure.

The simplistic biogeochemistry-ocean model, CSIRO-Mk3L, demonstrated a large future ocean saturation state sensitivity to enhanced organic carbon export and reduced carbonate export. The low-latitude sub-surface and abyssal ocean regions showed particular sensitivity to the combined contribution of the dual feedbacks of varying elemental and rain ratios. As carbonate saturation is a commonly accepted proxy for calcification, such a sensitivity has relevance for predicting changes in ecosystem dynamics in an increasingly acidic marine environment. However, this model did not resolve sedimentary carbonate compensation, which is a significant actor in marine carbonate chemistry over the timescale considered.

The limitations of the CSIRO-Mk3L model (instant sinking and dissolution of CaCO_3 , lack of sedimentary carbonate compensation or explicit biology) are not present in the more complex University of Victoria Earth System Climate Model (UVic ESCM), which was modified with the inclusion of a calcifying phytoplankton functional type, a full calcite tracer, carbonate chemistry dependent calcite dissolution rates, and a ballasting scheme. These modifications slightly improved UVic ESCM performance with respect to observed carbon and nutrient fluxes while significantly improving the mechanistic realism of the model. Further addition of a carbon-

ate chemistry dependency on calcifier microbial recycling rates in the UVic ESCM improved calcifier biogeography, but produced mixed results with respect to overall model skill at reproducing various observed ocean metrics. Unfortunately, there is very little in the scientific literature regarding both calcifier-specific microbes' response to acidification, and calcifier sensitivity to microbial degradation under acidification, so this exercise was mostly speculative. One limitation of the UVic ESCM is that unlike the CSIRO-Mk3L, the code structure is not easily amenable to flexible carbon and nutrient ratios. It would have been interesting to implement the same modifications made to CSIRO-Mk3L in the UVic ESCM to more directly compare the effect of sedimentary carbonate compensation, but unfortunately this would have required a major restructuring of the model code.

Greenhouse gas forcing of four variations of the UVic ESCM (1: without calcifiers, 2: with calcifiers, 3: with calcifiers and prognostic CaCO_3 , and 4: with calcifiers, prognostic CaCO_3 , and chemistry-dependent calcifier microbial recycling) showed a common response of a transition between two dominating biogeochemical feedbacks. The first is a physically driven one that dominated at lower changes in sea surface temperatures (SSTs) that is sensitive to phytoplankton community composition. The second overtakes the first at higher SST changes and is controlled by biology through warming-enhanced remineralisation rates. The deep ocean carbon export and oxygen response was found to be highly sensitive to the inclusion of a prognostic calcite tracer in this second feedback, because ballasting of POC by CaCO_3 increased over the simulations, reducing the amount of remineralisation occurring in the near-surface. Reduced CaCO_3 export by phytoplankton calcifiers in the 4th model configuration had little overall effect on ocean carbonate saturation since the zooplankton calcifier CaCO_3 export increased over the same time period and sedimentary carbonate compensation maintained ocean carbonate chemistry.

These experiments underscore the urgency of adequately constraining ocean biogeochemical models. Potentially large changes in global NPP, carbon uptake, and oxygen are looming in the coming decades that could have major ecological consequences. Calcifiers as a phytoplankton functional type occupy an important carbon cycle role as potentially effective detritus exporters that can mitigate warming-enhanced remineralisation feedbacks. However, their biogeography positions them in the regions affected earliest by warming-enhanced remineralisation, which increases the overall system sensitivity to changes in SSTs. Indications are their populations are due to expand over the coming decades, though any benefits in terms of carbon export will be offset by eventual enhanced microbial activity if strong anthropogenic warming is allowed to occur, and potentially also by weakening of the ballast effect

by acidification. Calcifiers in the UVic ESCM simulations also act as gatekeepers for nutrient fluxes to the Southern Ocean, and are able to effectively prevent the extreme increases in NPP and deoxygenation that occur there in the model without calcifiers. These model calcifiers are barely representative of actual calcifiers because they are tuned mainly to one species (*E. huxleyi*) and pathetically sparse datasets. The gatekeeper role identified here could just as easily be assigned to another non-calcifying phytoplankton type with high nutrient affinities, or might not exist at all since a recent model-data hindcast indicates globally declining NPP. Establishing the likelihood of a Southern Ocean nutrient exchange developing in the real world is of high importance because of the deoxygenation implications under the microbe-dominated high SST feedback. Furthermore, the strength and global sensitivity of the temperature dependency of biological processes urgently needs to be better constrained since its onset represents a potential tipping point for ocean NPP.

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