Dissolved Oxygen in the Oceans: An Examination of the Late Ordovician and the Near Future Using an Earth System Climate Model

DISSERTATION

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Abstract

One of the largest ecosystem controls in the oceans is the presence of dissolved oxygen. As oxygen levels fall, both micro- and macroorganisms face shrinking habitats and potential mortality. There have been several periods in Earth history where oxygen levels have fallen to anoxic (dissolved O\textsubscript{2} concentration < 10 μmol L\textsuperscript{-1}) or hypoxic (< 60 μmol L\textsuperscript{-1}) levels in certain ocean basins or within inland seas and some of these events could potentially be linked to mass extinction events. Several hypotheses exist regarding the depletion of oxygen, the spread of hypoxia-anoxia, and why the low oxygen events occur at certain points in the geologic record, including rapid climate warming, enhanced nutrient inputs, and modifications to the surface biological pump. Unfortunately, there is little agreement on which of these potential hypotheses caused individual events and what might impact the oxygenation of our oceans in the future.

This dissertation will test hypotheses related to deep ocean oxygen using the University of Victoria Earth System Climate Model. The first set of experiments feature Late Ordovician winds and paleogeography and test the impacts of atmospheric CO\textsubscript{2} and O\textsubscript{2}, ocean bottom topography, and nutrient loadings on deep ocean oxygen concentrations. The second set of experiments is also within the Late Ordovician, but tests the impacts of remineralization rates, detrital sinking velocities, and ocean surface albedo on ocean oxygenation. The final set of experiments tests the impacts of a warming
climate on the oxygenation of near-future oceans, in addition to the impacts of detrital sinking velocities and ocean surface albedo.

For the Late Ordovician, the factors most favorable for the spread of anoxia are reduced atmospheric O$_2$, increased loadings of nitrate, and a reduction in ocean surface albedo. Climatic factors (namely, increased CO$_2$) played little role in the spread of anoxia or the depletion of oxygen in these experiments. Similarly, phosphate, enhanced remineralization rates, and slower sinking velocities do little to diminish the dissolved oxygen, but can actually work to increase oxygen below the surface layer, potentially based on where the remineralization is occurring due to these modifications.

The future oceans will be impacted by warming; the largest reductions in ocean oxygen can be attributed to decreased dissolution of atmospheric oxygen in warmer surface waters. Shrinking sizes of particles (done here by reducing particle velocities) may actually work to counteract some of the reductions in ocean oxygen due to climate warming, as fewer particles fall into the deep ocean, reducing deep remineralization and uptake of oxygen.
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Chapter 1. Introduction

Dissolved oxygen in the oceans is arguably one of the most critically important components to maintaining marine ecosystems. With the exception of some recently discovered extremophiles, all benthic and pelagic macroorganisms require oxygen. Regions that experience declining levels of dissolved oxygen can rapidly lose habitability for many species, forcing them to migrate and relocate or die altogether. When dissolved oxygen falls below certain thresholds for life ($< 60 \mu\text{mol L}^{-1}$), we call these regions hypoxic ($\sim 50\%$ mortality for marine benthic animals) or anoxic ($\sim 90\%$ mortality for marine benthic animals) [Deutsch et al., 2011].

The earliest oceans on Earth were likely anoxic, as the atmosphere had almost no oxygen during Earth’s early history. While it is unclear whether oxygen co-accumulated in the atmosphere and oceans in the Precambrian or if the accumulation of oxygen in the atmosphere led to the accumulation of oxygen in the oceans, the evolution of marine life and, eventually terrestrial life, became more complex as oxygen reached threshold levels in the Cambrian (~541-485 million years ago[ma]) [Butterfield, 2009].

Geological evidence for intermediate and deep ocean anoxia exists for several time periods in the Phanerozoic, including the Late Ordovician-Early Silurian [Melchin et al., 2013], Permian-Triassic [Wignall and Hallam, 1992; Montenegro et al., 2011], and Mid-Cretaceous [Jenkyns, 1980; Misumi and Yamanaka, 2008; Monteiro et al., 2012];
three time periods of mass extinction where anoxia might have been one of the mortality mechanisms for many species. While these events are generally well recorded by isotopic excursions and organic-rich black shales, and have been simulated in various modeling efforts, the exact causes of low oxygen events still remain an open question. Generally speaking, warmer climatic conditions reduce the dissolution of atmospheric oxygen in ocean waters [Garía and Gordon, 1992; Deutsch et al., 2011]. Warmer climates also favor a reduction in deep ocean overturning, reducing the ventilation of the intermediate and deep oceans, reducing their exposure to the atmospheric source of oxygen [Sarmiento et al. 1988; Deutsch et al., 2011]. Lower concentrations of atmospheric oxygen tend to amplify all of these climate-related causes of hypoxia-anoxia [Butterfield, 2009; Melchin et al., 2013] as less is available to be dissolved in ocean waters.

Although climate changes can drive hypoxia-anoxia, several model studies have shown that biological and biogeochemical factors are also important for maintaining and expanding low oxygen conditions. For example, surface eutrophication leads to increases in surface primary production and respiration, creating more detritus which is remineralized as it falls through the water column, consuming oxygen. This can initiate a positive feedback loop, as remineralization can lead to enhanced return of phosphate (PO₄) to the surface, enhancing primary production, and consuming more oxygen [Van Cappellen and Ingall, 1994; Tsandev and Slomp, 2009]. This alteration of the biological pump can lead to proliferation of cyanobacteria, which are smaller than the dominant eukaryotic phytoplankton today, leading to water column stratification and enhanced remineralization, further reducing oxygen concentrations [Butterfield, 2009].
There are multiple potential causes for the development and spread of low dissolved oxygen conditions in the ocean, but mechanisms vary and each situation is unique. This dissertation has two main goals, which are examined in three distinct sets of experiments. The first goal is to test potential causes of relatively widespread anoxia during a time of extensive environmental change, the Late Ordovician, a time not well-modeled for deep ocean anoxia. The second goal is to examine the impacts of a warming climate and rapid environmental changes on the oxygen concentrations of future oceans. Testing these two time periods with a variety of variable modifications serves to test multiple potential causes for low oxygen events in changing climates. All three sets of experiments for this dissertation relied upon the University of Victoria Earth System Climate Model (UVic ESCM) \cite{Weaver2001}, a model of intermediate complexity featuring a full ocean general circulation model \cite{Pacanowski1995} and a sophisticated marine ecosystem and carbon cycle model \cite{Schmittner2008}.

The first set of experiments examined the impacts of varying solar constants, atmospheric CO$_2$, atmospheric O$_2$, winds, ocean bathymetry, and nutrient loadings on deep ocean oxygen with Ordovician paleogeography under high sea level \cite{Herrmann2004}. To test the impact of climate, we used two solar constant values, a present day and one more representative of the Late Ordovician according to stellar evolution models \cite{Endal1981}. Additionally, we tested two levels of atmospheric CO$_2$ concentration based on the work of Berner \cite{Berner2006}: 8x preindustrial atmospheric levels (PAL, 2240 ppmv) and 12xPAL (3360 ppmv). Berner \cite{Berner2006} also provided ranges of atmospheric O$_2$ to be tested, as the Ordovician was generally believed to have a lower O$_2$
concentration (~10%-18% atmospheric volume) than present (21% by volume). We tested atmospheric O$_2$ levels of 12% and 8% (see Berner [2006], Bergman et al. [2004], and Chapter 2 for further reasoning on these levels of O$_2$). Two sets of winds and bottom topographies were used to determine if atmospheric or oceanic dynamics impact the uptake of oxygen and the spread of anoxia. Lastly, the concentrations of two macronutrients, PO$_4^{3-}$ and nitrate (NO$_3^-$) were doubled to determine if eutrophication might have played a role in Ordovician anoxia.

The second set of experiments tested the impacts of atmospheric O$_2$, remineralization rates, settling velocities, and ocean albedo on Late Ordovician deep ocean oxygen. The same two values of O$_2$ from the first set of experiments were used, but this time they were each spread across each experiment. In order to test the positive remineralization feedback of Van Cappellen and Ingall [1994], remineralization rates were set to 1.5x the present-day values. Initial values of settling velocity were reduced by half (from present day) in order to test if smaller (and therefore slower settling) particles have a profound impact on deep ocean O$_2$ [Butterfield, 2009]. The albedo of the oceans was also reduced by 0.09 to see if a darker (i.e., more turbid) water column would increase stratification, and enhance the uptake of dissolved oxygen [Butterfield, 2009].

The final set of experiments tested the impacts of climate changes and stratification on future intermediate and deep ocean oxygen. Three levels of atmospheric CO$_2$ were utilized: a constant value of 280 ppmv (preindustrial), a constant value of 400 ppmv (a value representative of 2016/2017), and a business-as-usual emissions scenario starting from 2015 that is reminiscent of an Intergovernmental Panel on Climate Change
(IPCC) A2 scenario [Nakicenovic et al., 2000]. Additionally, settling velocities and albedo were reduced to test if the Butterfield [2009] and Mouw et al. [2016] hypotheses could have the potential to initiate or spread intermediate ocean hypoxia-anoxia.

Each section of this dissertation (with the exception of the conclusion) outlines one of the above sets of experiments in greater detail, including more introductory material, methods, results, and discussion for each problem tested over the course of this research. Each section is formatted as a manuscript ready to be submitted as an American Geophysical Union style journal article, as that is the style I (along with my advisor) have chosen for this research. The goal is to have each one of the next three sections submitted and published in a peer-reviewed journal in the next year and a half. To avoid copyright infringement on my work, I will make minor changes to each section so that they are not exact duplicates of the papers submitted to journals.
Chapter 2. Ordovician climate simulations with an Earth system model: Impact of atmospheric O₂ and CO₂, bottom topography, and nutrient inputs on deep ocean oxygen concentrations

2.1. Chapter 2 Introduction

The Ordovician (485-444 Ma) was marked by high atmospheric CO₂ concentration (~4-18x preindustrial levels) and rapid climatic and ecological changes including two pulses of mass extinction around the Hirnantian (445-444 Ma). The Early Ordovician (485-470 Ma) began with a boom in biodiversity known as the Great Ordovician Biodiversification Event (GOBE), which features a significant increase in biodiversity of marine benthos and phytoplankton, as well as the development of a diverse zooplankton assemblage [Servais et al., 2010]. In addition to the diversification of life in the oceans, the first evidence for non-vascular land plants began in the Middle Ordovician (470-458 Ma) [Vecoli et al., 2011; Lenton et al., 2012; Porada et al., 2016].

The increase in chemical weathering due to the appearance of land plants and possibly from the easily weathered, young rocks of the Taconic Orogeny [Berner, 2006], likely increased nutrient runoff into the oceans [Porada et al., 2016]. The rise in ocean productivity associated with this extra nutrient input, in conjunction with the Boda Warming Event (BWE, 447-445 Ma), have been identified as potential causes for the large-scale ocean anoxia recorded in pre-Hirnantian marine sediments [Armstrong et al.,

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1 Coauthors: Alvaro Montenegro, Michael J. Melchin, and Michael Eby, submitted to Paleoceanography
2009b; Melchin et al., 2013]. The presence of plants in the Late Ordovician (458-444 Ma) has also been associated – through increased chemical weathering and uptake of atmospheric CO$_2$ – with cooling that contributed to the Hirnantian glaciation [Lenton et al., 2012; Porada et al., 2016]. The environmental change prior to the Hirnantian and the cooling during the Hirnantian contributed to the first wave of extinction, where faunal species were more likely to become extinct (particularly benthic species) [Melchin et al., 2013; Harper et al., 2014; Sheets et al., 2016].

Following the Hirnantian glacial period, euxinia and anoxia may have developed as sea levels began to rise, killing many of the survivors of the first extinction pulse [Melchin et al. 2013]. Both phases of the mass extinction can be potentially linked to anoxia and the glaciation [Hammarlund et al., 2012], as both events would have shifted habitable zones for certain species, forcing either mass marine migration or extinction. Rorhssen et al. [2013] and Melchin et al. [2013] also suggested linkages between the extinction events and the communities of bacterial and algal primary producers; around the time of the extinction events, nitrogen isotopes suggest primary production was reliant on nitrogen fixed by cyanobacteria [LaPorte et al., 2009], a smaller phytoplankton which is susceptible to very low settling rates [Butterfield, 2009]. The Late Ordovician extinctions were responsible for the estimated disappearance of 85% of marine animal species and 25% of animal families and disrupted the GOBE. Recovery did occur following the Late Ordovician, but biodiversity plateaued until the Permian-Triassic extinction event (~252 Ma) [Harper et al., 2014].
Physical evidence for anoxia exists in many locations globally, mainly in the form of Ordovician aged, organic-rich black shales in Late Katian (~453-445 ma) and earliest Silurian time (444 ma) [Armstrong et al., 2009a; Berry, 2010; Thompson and Kah, 2012; Melchin et al., 2013]. Although the physical evidence that oceanic anoxia was more restricted in marine shelf and slope environments during the Hirnantian glacial interval [Melchin et al., 2013], there is controversy surrounding the extent of anoxia in the bathyal and abyssal parts of the oceans during the peak of the glaciation [e.g., Hammarlund et al., 2012; Melchin et al., 2013; Jones and Fike, 2013]. Isotopic evidence also suggests that oceanic primary production might have increased during periods in the Ordovician [Saltzman 2005]. Several potential factors might have contributed to the proliferation of anoxia within the Late Ordovician. Six such causes are discussed in Melchin et al. [2013]: 1) hydrographical setting of the marine basin; 2) changes in sea level and climate; 3) rate of nutrient input into the oceans; 4) rate of nutrient recycling within the oceans; 5) atmospheric oxygen levels; and 6) changes in the biosphere. Factors 1) and 2) can both be related to circulation and ventilation, particularly for shallow basin and inland sea settings. Factors 3), 4), and 6) are related to increases in primary production and subsequent increases in oxygen uptake during respiration and export and burial of organic matter leading to the formation of the organic-rich black shales mentioned above. Oxygen uptake is further enhanced when organic matter falls more slowly through the water column due to sluggish ocean circulation or a reduction in particle size [Butterfield, 2009]. Factor 5) is related to relatively low atmospheric oxygen concentrations during the time period [Berner, 2006], which can be directly linked to
oxygen saturation in seawater with the equations described in *García and Gordon* [1992]. Despite the geological evidence and many suggested processes, no consensus presently exists on the probable causes of Ordovician bottom anoxia [*Melchin et al.*, 2013]. Here we test the likelihood of some of these potential anoxia generating mechanisms using numerical simulations with an Earth System Climate Model covering the time period of interest.

2.1.1. Modeling studies of the Ordovician

Earlier numerical modeling efforts for the Ordovician have been primarily concerned with understanding the potential roles of paleogeography [*Nardin et al.*, 2011; *Pohl et al.*, 2014], atmospheric CO$_2$ [*Gibbs et al.*, 1997; *Poussart et al.*, 1999; *Herrmann et al.*, 2004a, b; *Pohl et al.*, 2016a, b], and orbital forcing [*Herrmann et al.*, 2003] on the initiation of the Hirnantian glaciation. The initiation of glaciation transpired despite high CO$_2$ concentrations between about 4-14x pre-industrial atmospheric levels (PAL, where PAL = 280 ppm). While previous studies have addressed oceanic processes such as the location of oceanic gyres and upwelling regions [*Servais et al.*, 2014] and heat transport by the meridional overturning circulation (MOC) [*Herrmann et al.*, 2004b], there appear to be no results in the literature of simulations specifically designed for the analysis of O$_2$ distribution and the potential development of oceanic anoxia during the period.

2.1.2. Modeling ocean bottom anoxia

It has been proposed that in a greenhouse world warmer temperatures limit the solubility of oxygen in the water column [*García and Gordon*, 1992] and would contribute to oceanic anoxia, but such a process has not been reproduced well by
simulations in the deep oceans, nor has the expansion of low oxygen conditions below the thermocline. High CO$_2$ concentrations on their own did not lead to deep ocean anoxia in numerical simulations of the Permian-Triassic boundary [Montenegro et al., 2011], with the causes potentially linked to extreme volcanism. Ozaki et al. [2011] used a one-dimensional ocean biogeochemical model to simulate oxygen distribution under high atmospheric CO$_2$ conditions and concluded that a slower overturning circulation, coupled with lower solubility of oxygen alone was unable to cause deep ocean anoxia. The same authors found that an elevated flux of reactive phosphorus is the most important factor for triggering anoxia, through a positive feedback loop with ocean anoxia, P regeneration, and surface biological productivity [Ozaki et al., 2011]. The main drawback, in the context of this research, is that the Ozaki et al. [2011] simulations were not conducted with a full ocean general circulation model (OGCM). Monteiro et al. [2012] also show a similarly decisive contribution of nutrient loading on the spread of anoxia in the Cenomanian-Turonian ocean anoxia event.

Misumi and Yamanaka [2008] used a full three-dimensional OGCM coupled with a biogeochemical model in an attempt to reproduce anoxic conditions under a Cretaceous climate state. Once again, anoxia could not be forced by a slowing of the MOC or circulation alone, but needed an acceleration of biogeochemical processes via increases in phosphate input to the oceans. Monteiro et al. [2012], Montenegro et al. [2011], Ozaki et al. [2011], and Misumi and Yamanaka [2008] all agreed with previous work stating that changes in biological or biogeochemical processes are necessary for generating widespread anoxia [Meyer et al., 2008]. Like the Permian-Triassic, the Cretaceous was
quite different from the Ordovician with different paleogeography, but perhaps more importantly, with the presence of vascular land plants during the younger periods. No evidence of vascular land plants exists for the Ordovician, although lichens and bryophytes were likely widespread.

2.1.3. The study

This research addresses the lack of climate modeling studies focusing on the Late Ordovician oceans using the University of Victoria Earth System Climate Model (UVic ESCM) [Weaver et al., 2001]. An outline of the rest of the paper is as follows: the next section will present the model and the various modifications needed for a set of experiments designed to test some of the hypotheses regarding Late Ordovician anoxia. The third section features an analysis of our control simulation. The fourth section features results from selected experiments. The fifth section will highlight the results with regards to the hypothesized causal factors of Melchin et al. [2013], and the final section presents the conclusions.

2.2. Methods

This study utilizes the UVic ESCM version 2.9, a model of intermediate complexity. The ocean component is the Geophysical Fluid Dynamics Laboratory (GFDL) Modular Ocean Model (MOM) version 2.2 [Pacanowski, 1995], which is based on the Navier Stokes equations subject to the Boussinesq and hydrostatic approximations. This three-dimensional OGCM is capable of representing horizontal ocean gyre transport and deep convection processes, which are fundamental for the MOC. The MOM within the UVic ESCM has a spatial resolution of 3.6° longitude by 1.8° latitude, with 19
vertical levels to a depth of 6000 m. Ocean surface temperatures initialize at 21.6°C near the equator, decreasing polewards to values around 16.4°C at 40°N/S and 2.3°C near the poles. Subsurface temperatures decrease with depth to a value of 2°C globally. Salinity initiates with a global (surface and subsurface) value of 34.7‰.

Coupled to the full OGCM is a thermodynamic/dynamic sea ice model [Hibler, 1979; Hunke and Dukowicz, 1997; Bitz et al., 2001], allowing for atmosphere-ocean-sea ice coupling. The sea ice model has the ability to represent sea ice dynamics with various options for sea ice thermodynamics and thickness distribution. The ocean component is coupled to a two dimensional (vertically averaged) energy-moisture balance model (EMBM) [Fanning and Weaver, 1996]. Atmospheric heat and water transports are parameterized through advection and Fickian diffusion. Precipitation is assumed to occur when relative humidity exceeds 85% [Weaver et al., 2001]. The EMBM also features parameterizations of radiative transfer including longwave feedbacks from water vapor and CO₂. Because atmospheric dynamics are not explicitly resolved, winds need to be prescribed. Land-atmosphere energy and mass fluxes are calculated by the United Kingdom Met Office Surface Exchange Scheme land surface model [Best et al., 2011; Clark et al., 2011]. All coupling of the individual models is done through a dynamic coupler. The simple atmosphere component allows the use of complex ocean and ecosystem models to conduct the multiple, long (several thousand years) simulations required to meet the goals of this investigation. Given the rapidly changing dynamics of the atmosphere system and the need for complicated parameterizations of atmospheric
processes, large-scale simplification of the atmosphere allows for additional computational affordability.

The ocean ecosystem model is an improved NPZD (nutrient, phytoplankton, zooplankton, detritus) representation from Schmittner et al. [2005] which features a full representation of the carbon cycle, unlike the initial model [Schmittner et al., 2008]. Phosphate (PO$_4$) and nitrate (NO$_3$) are the featured nutrients. Initial surface concentrations of PO$_4$ are around 0.5 $\mu$mol L$^{-1}$ at the equator, gradually increasing to a 2 $\mu$mol L$^{-1}$ peak just outside of the poles (around 75°N/S). Subsurface concentrations of PO$_4^{3-}$ below the photic zone have global values around 2 $\mu$mol L$^{-1}$. Initial concentrations of NO$_3^-$ exhibit a similar pattern, but with surface values of 4 $\mu$mol L$^{-1}$ around the equator increasing to a peak of 25 $\mu$mol L$^{-1}$ near the poles (~75°N/S), and subsurface values of 30 $\mu$mol L$^{-1}$. Model net primary production (NPP) is a function of surface chlorophyll content, light supply, and temperature. More on the calculation of NPP as a model product can be found in Appendix A of Schmittner et al. [2008]. Tracers (variables that can track changes to various ocean systems) include O$_2$, dissolved inorganic carbon (DIC), and alkalinity [Schmittner et al., 2008]. Dissolved O$_2$ begins with a global initial value of 170 $\mu$mol L$^{-1}$ (surface and subsurface below the oxygen minimum zone). Inorganic tracers and the nutrients PO$_4$ and NO$_3$ are connected by changes in inorganic nutrients and calcium carbonate. DIC and alkalinity are controlled in the marine carbon cycle model by changes in inorganic nutrients and calcium carbonate.
As this study is focused on anoxia, the modeled sources and sinks of O\textsubscript{2} become very important. In the model, oxygen and other biogeochemical variables have their concentration, C, change over time, t, according to:

\[
\frac{\partial C}{\partial t} = T + S
\]  

(2.1)

where T represents all transport terms including advection, diffusion, and convection, and S denotes source minus sink terms. For O\textsubscript{2}, S is described by

\[
S(O_2) = F_{sf} - S(PO_4)R_{O:P}r_{SOX}^{O_2}
\]  

(2.2)

where \(F_{sf}\) is the surface layer dissolved O\textsubscript{2} exchange with the atmosphere, \(S(PO_4)\) are the sources and sinks of phosphate, \(R_{O:P}\) represents the constant Redfield ratio of oxygen to phosphorus, and \(r_{SOX}^{O_2}\) is the oxygen consumption in suboxic waters [Schmittner et al., 2008]. Detritus is remineralized in the water column through the following relationship:

\[
\mu_D = \mu_{D_0} \exp \left( \frac{T}{T_B} \right) \left[ 0.65 + 0.35 \tanh(O_2 - 6) \right]
\]  

(2.3)

where \(\mu_D\) is the remineralization of detritus, \(\mu_{D_0}\) is the initial remineralization rate (0.048 day\(^{-1}\)), \(T\) is the water temperature in °C, \(T_B\) is the e-folding temperature of biological rates (15.65°C), and \(O_2\) is the concentration of dissolved oxygen in μmol. Denitrification consumes NO\textsubscript{3} at a rate of 80% of the oxygen equivalent rate, as NO\textsubscript{3} is a more efficient oxidizer on a mole per mole basis than O\textsubscript{2}. As more oxygen is consumed in the water column, rates of denitrification and NO\textsubscript{3} uptake increase [Schmittner et al., 2007a].

2.2.1. Paleogeography

Land distribution comes from the high sea level Katian (Caradoc-Ashgill - 454-444 Ma) configuration described in Herrmann et al. [2004a, b] and based on
reconstructions from *Scotese and McKerrow* [1990; 1991] and *Scotese* [1997]. Evidence for high sea level exists in the Middle and Late Ordovician, with wide areas of continental blocks flooded [*Herrmann et al.*, 2004b]. High sea level stands varied between 175-600 m [*Vail et al.*, 1977; *Hallam*, 1984; *Algeo and Seslavinsky*, 1995a, b] above modern sea level. General agreement exists for the location of the three major paleocontinents during the period: Gondwana, Laurentia, and Baltica, along with minor agreement for Siberia, but several other terranes of near continental size (such as South China) are loosely constrained and their precise location is unknown [*Torsvik and Cocks*, 2013]. Additionally, some modest size terranes are unidentifiable at this time, increasing uncertainty in paleocontinental placement [*Torsvik and Cocks*, 2013]. As in all other versions of UVic ESCM, artificial islands are added at 90°N and 90°S to eliminate grid convergence and avoid numerical instabilities. Essentially these islands are completing the model grid so that, unlike with longitude, information is not fed directly from 90°N to 90°S and vice versa.

The ocean bottom is set at the 17th vertical level, about 4657.5 m deep. Part of the reason this is done is to maintain an ocean volume similar to the present day, which the model favors. This means larger-than-present ocean volumes create numerical instabilities, which can and will render model results useless. Bathymetry (Fig. 2.1) is similar to the one adopted by *Herrmann et al.* [2004b] and based on the same tectonic models used for the land distribution [*Scotese and McKerrow*, 1990; 1991; *Scotese*, 1997]. Due to the high sea stand, continental shelves are placed around 400 m depth, as
in Herrmann et al. [2004]. Flat ocean bottom experiments are conducted at the 16th vertical layer (4142.5 m).

**Figure 2.1:** Late Ordovician paleogeography, ocean bottom topography (meters below sea level), color fill), and wind stress vectors (Pa, orange arrows, reference vector 0.08 Pa) adopted in the simulations.

As no land surface topographic maps have been published for the Late Ordovician, all land bins are set to an elevation of 0 m above sea level, an approach that has already been adopted by earlier modeling efforts [Crowley and Baum, 1995; Gibbs et al., 1997; Herrmann et al., 2003; 2004a, b]. Runoff is calculated for every land mass, but as it is impossible at present to determine the location of rivers, runoff is equally distributed around continents and islands, which can eliminate regional sources of eutrophication and potentially anoxia. The land surface has bare rock with no vegetation
cover, due to the very limited information on Ordovician land cover. The first land plants likely appeared in the mid-Ordovician [Lenton et al., 2012], but they were non-vascular. While these early plants may have impacted P input into the oceans, P fluxes in the adopted NPZD model are prescribed for enhanced nutrient simulations (described below in Section 2.2.5) and are not dependent on vegetation cover. All land points that are not ice or snow covered are assigned surface albedo value of 0.3.

2.2.2. Winds

As stated above, the UVic ESCM does not explicitly resolve atmospheric dynamics and winds must be prescribed. The adopted wind fields are based on wind stress data generated by the fully coupled simulations of Herrmann et al. [2003]. To the best of our knowledge, these data were not publicly available and were provided to us. These data are now archived in D’Amico et al. [2017]. Wind data required by the UVic ESCM were calculated using:

\[ \tau = C_D \rho_{air} |V_S| \bar{V}_S \]  

(2.4)

where \( \tau \) is the wind stress, \( C_D \) is the dimensionless drag coefficient with a constant value of 0.0014, \( \rho_{air} \) is the density of air (1.22 kg m\(^{-3}\)), and \( |V_S| \) and \( \bar{V}_S \) are the absolute value of the surface winds and the surface wind vectors, respectively. The annual average of winds was utilized for the entirety of each simulation. Figure 2.1 shows the surface wind stress vectors (shear stress exerted by winds on large bodies of water) and paleogeographic reconstruction, including bathymetry, used in our UVic ESCM simulations. Wind stress values and surface advecting winds are reduced by 20% in experiments that test if ocean bottom oxygen is impacted by varied wind intensity. Apart
from the reduced wind field, all simulations, regardless of radiative forcing, will feature the same wind fields as we only had one dataset of winds available.

Wind stress patterns were generally similar to those seen today. Weak easterlies exist around the equator with weak meridional convergence, suggesting the average location of the intertropical convergence zone (ITCZ). The location of this ITCZ was in relative agreement with the location of the ITCZ in the geochemical study of Armstrong et al. [2009b], particularly for the Early BWE and the Hirnantian. The subtropics for both hemispheres showed generally divergent wind stress, with vectors becoming more westerly in the mid-latitudes. Subtropical high circulations do not exist, likely due to varied deflection from the paleocontinental configuration relative to the present day. The Polar Regions show another shift to weak easterlies. In the southern hemisphere, there also appeared to be two cyclonic circulations similar to the Aleutian and Icelandic Lows seen in the present day Northern Hemisphere. Due to the lack of landmasses in the Northern Hemisphere, these semi-permanent circulations are much more diffuse. A large-scale circumpolar circulation exists south of 60°N, similar to the circumpolar circulation around present day Antarctica.

2.2.3. Radiative forcing

The time scale of Milankovitch cycle orbital forcing variability (~10^4 to 10^5 yrs) is at least one order of magnitude shorter temporally than what is indicated by the geological record of widespread deep bottom anoxia events in the Late Ordovician. With this in mind, orbital parameters were kept constant at present day values. In our simulations the radiative forcing is changed through prescribed atmospheric CO₂
concentrations and changes to the solar constant. While the Ordovician atmospheric concentration of CO$_2$ is under some debate, there is general consensus that it was higher than PAL [Berner, 2006]. Different studies have adopted CO$_2$ concentrations for the period ranging from 4xPAL [Pohl et al., 2014] to 18xPAL [Herrmann et al., 2004b] based on differing geochemical evidence [Bergman et al., 2004; Berner, 2006]. Here we conduct experiments with three levels of atmospheric CO$_2$: 4xPAL (1120 ppm), 8xPAL (2240 ppm), and 12xPAL (3360 ppm). Two solar constants were utilized, 1368 W m$^{-2}$ (present day value) and ~1313 W m$^{-2}$, where the solar constant is reduced to that theorized for the Late Ordovician, around 96% of the present day value [Endal and Sofia, 1981; Crowley and Baum, 1995].

2.2.4. Atmospheric oxygen

The concentration of oxygen in the atmosphere has an influence on the oxygenation of the ocean bottom [García and Gordon, 1992; Archer et al., 2004; Berner et al., 2007; Ozaki et al., 2007]. Atmospheric O$_2$ concentration is also an important consideration to the Redfield ratio for phytoplankton growth [Lenton and Watson, 2000a, b]. While significant uncertainty still exists regarding Paleozoic atmospheric oxygen concentrations, there is consensus that these were lower than the present day value of ~20.95% by volume. Some studies have suggested a mid-Ordovician range of 10-17% by volume [Berner, 2006] while others propose a lower boundary at ~5% by volume [Bergman et al., 2004]. We conduct experiments with two distinct concentrations of 12% and 8% by volume.
Atmospheric O$_2$ is not explicitly tracked by the UVic ESCM atmospheric model and hence O$_2$ concentration cannot be directly changed in the model’s code. In order to circumvent this issue, a modification is made to the following equation for oxygen saturation in the oceans from García and Gordon, [1992]:

\[
\ln C_0^x = A_0 + A_1 T_S + A_2 T_S^2 + A_3 T_S^3 + A_4 T_S^4 + \\
A_5 T_S^5 + S(B_0 T_S + B_2 T_S^2 + B_3 T_S^3) + C_0 S^2
\]  

(2.5)

where $C_0^x$ is the solubility of O$_2$ per unit mass or per unit volume at the temperature of equilibrium. The subscript, $O$, denotes O$_2$ while the $x$ superscript signifies equilibrium with an atmosphere of standard composition saturated with water vapor at a total pressure of 1 atm. $A_i$ and $B_i$ are constant coefficients, $C_o$ without the $x$ superscript is a constant coefficient, $S$ represents the salinity in per mil (‰), and $T_s$ is a scaled temperature as follows:

\[
T_S = \ln[(298.15 - t)(273.15 + t)^{-1}]
\]  

(2.6)

with $T_s$ expressed in K and $t$ being the water temperature in °C.

The change in atmospheric O$_2$ concentration is obtained by multiplying Equation (2.5) by a constant with a value of 0.382 for the 8% O$_2$ experiments and with a value of 0.573 for the 12% O$_2$ experiments. This assumption can be made because the value of $C_0^x$ is linearly related to the mole fraction of O$_2$ in dry air through the following relation:

\[
C_0^x = 0.20946F(1 - P_{wv})(1 - B_0)(K_0 M_w)^{-1}
\]  

(2.7)

where $F$ and $M_w$ are a salinity factor and the gram molecular mass of water, respectively. $B_o$ is a constant coefficient and the constant 0.20946 is the mole fraction of O$_2$ in dry air.
Equation (2.7) is not represented directly in the UVic ESCM code but is implicit in Equation (2.5), which is present.

2.2.5. Nutrients

Increases in primary production at the ocean surface and just below the ocean surface contribute to near surface depletion of dissolved CO$_2$ and enhancement of dissolved O$_2$ due to photosynthesis. Below these upper ocean levels, CO$_2$ concentration will slowly increase and O$_2$ concentration will slowly decrease due to respiration and oxidation of detritus. More NPP further depletes dissolved O$_2$ in the oxygen minimum zone, but the MOC, diffusion, and advection deliver oxygen from the surface to the deep oceans, limiting the spread of bottom hypoxia or anoxia. However, enhancement of NPP, by enhanced nutrient inputs, recycling, or both, will increase the detrital products falling to the ocean bottom, which will continue to be oxidized, further depleting O$_2$.

A series of earlier simulation efforts for varying times indicate that expansive anoxia cannot be modeled simply through changes in ocean dynamics due to climate change [Misumi and Yamanaka, 2008; Montenegro et al., 2011; Ozaki et al., 2011; Monteiro et al., 2012]. It has also been suggested that widespread bottom anoxia requires changes to the biogeochemistry of upper layers [Butterfield, 2009]. In this set of simulations, the sensitivity of bottom O$_2$ to biogeochemistry is evaluated through changes to nutrient flux into the ocean. The two macronutrients that impact oceanic primary productivity are PO$_4$ and NO$_3$. Falkowski [1997] pointed out that the nutrient with the largest control over marine primary production has been a long-standing debate in paleoceanography. Saltzman [2005] attempted to address this issue by examining positive
excursions in δ^{13}C from carbonates and concluded that different climate modes can shift the limiting nutrient between PO_4 and NO_3, in addition to limitation by trace metal nutrients. This work tested both possibilities, conducting experiments where the standard background concentrations of PO_4 and NO_3 were doubled at the beginning of the simulation and allowed to remain at this constant doubled value throughout the simulation period. This is also assuming that the ecosystem response to nutrients is similar to today, which has its risks, as there are many biological and evolutionary factors that could have been impacting ecosystems in Earth history. Testing this assumption is outside of the scope of this current research.

2.2.6. Experiments

The various experiments utilized in this study are shown in Table 2.1. The control simulation used for Appendix A (validation of the UVic ESCM Ordovician climate) adopts the reduced solar constant (Ctrl-RSC), while the simulations presented in the results section will feature the warmer, and hence potentially more anoxia friendly present day solar constant (PDSC). All simulations have the same paleogeography, sea level, and orbital parameters. The CO_2 concentration was slowly increased in the Ctrl-PDSC simulation so that the model could better adjust to the major increases in radiative forcing relative to the present day. Once at the final CO_2 value (12xPAL), the Ctrl-PDSC was run until ocean temperatures, ocean kinetic energy, and dissolved oxygen in the ocean stabilized (approximately 4000 years). All experimental simulations, including those with a reduction in CO_2, used initial conditions coming from the stable state of the Ctrl-PDSC experiment. Non-control simulations are run until stability in ocean kinetic
energy, ocean temperature, and ocean dissolved oxygen concentration. These simulations took between 4000 and 7000 years, depending on the variables modified for a given experiment.

Table 2.1: List of experimental simulations utilized for this research. Abbreviations and shorthands are as follows: xPAL = times preindustrial atmospheric level; xPD = times the present day value; Ctrl = control, RSC = reduced solar constant; PDSC = present day solar constant; Red = reduced, Min = minimum.

<table>
<thead>
<tr>
<th>Simulation</th>
<th>CO₂ Conc Units</th>
<th>Solar Const</th>
<th>O₂ Conc by volume</th>
<th>NO₃ Conc xPD</th>
<th>PO₄ Conc xPD</th>
<th>Winds % of Ctrl</th>
<th>Bathymetry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ctrl-RSC</td>
<td>12 xPAL</td>
<td>1313 W m²²</td>
<td>12</td>
<td>1</td>
<td>1</td>
<td>100%</td>
<td>Ridges/Shelves</td>
</tr>
<tr>
<td>Ctrl-PDSC</td>
<td>12 xPD</td>
<td>1368</td>
<td>12</td>
<td>1</td>
<td>1</td>
<td>100%</td>
<td>Ridges/Shelves</td>
</tr>
<tr>
<td>Red CO₂</td>
<td>8 1368</td>
<td>12</td>
<td>12</td>
<td>1</td>
<td>1</td>
<td>100%</td>
<td>Ridges/Shelves</td>
</tr>
<tr>
<td>Min CO₂</td>
<td>4 1368</td>
<td>12</td>
<td>12</td>
<td>1</td>
<td>1</td>
<td>100%</td>
<td>Ridges/Shelves</td>
</tr>
<tr>
<td>Red O₂</td>
<td>12 1368</td>
<td>8</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>100%</td>
<td>Ridges/Shelves</td>
</tr>
<tr>
<td>2xPO₄</td>
<td>12 1368</td>
<td>12</td>
<td>12</td>
<td>1</td>
<td>2</td>
<td>100%</td>
<td>Ridges/Shelves</td>
</tr>
<tr>
<td>2xNO₃</td>
<td>12 1368</td>
<td>12</td>
<td>12</td>
<td>2</td>
<td>1</td>
<td>100%</td>
<td>Ridges/Shelves</td>
</tr>
<tr>
<td>2xNO₃/PO₄</td>
<td>12 1368</td>
<td>12</td>
<td>12</td>
<td>2</td>
<td>2</td>
<td>100%</td>
<td>Ridges/Shelves</td>
</tr>
<tr>
<td>Red Wind</td>
<td>12 1368</td>
<td>12</td>
<td>12</td>
<td>1</td>
<td>1</td>
<td>100%</td>
<td>Ridges/Shelves</td>
</tr>
<tr>
<td>Ctrl-Flat</td>
<td>12 1368</td>
<td>12</td>
<td>12</td>
<td>1</td>
<td>1</td>
<td>100%</td>
<td>Flat</td>
</tr>
</tbody>
</table>

2.3. Analysis of Ctrl-PDSC

The results (Section 2.4) will feature comparisons between each of the experiments in Table 2.1 with the Ctrl-PDSC simulation, so this section will present a basic analysis of the simulation we have deemed to be our control simulation. Figure 2.2 shows the air temperatures and SSTs for Ctrl-PDSC. Both air temperatures (Fig. 2.2a) and SSTs (Fig. 2.2b) are warmer than most of the climate modeling studies of the Late Ordovician and those of the Ctrl-RSC (Figs. A.1-A.4), which is expected given the large differences in solar forcing among the different models. The intense forcing contributes
to wide swaths of air temperatures above 45°C (Fig. 2.2a) along the equator and most tropical waters are greater than 35°C (Fig. 2.2b), which is quite extreme relative to the present day and the Ordovician (Figs. A.1-A.4), but the extreme warmth might be a factor necessary for widespread anoxia in the UVic ESCM.

![Figure 2.2: a) Air temperatures (°C) for Ctrl-PDSC and b) sea surface temperatures (°C) for Ctrl-PDSC.](image)

Figure 2.3 shows the meridional overturning circulation (MOC) in Sv for Ctrl-PDSC and Ctrl-RSC. The MOC has a central role in climate by transporting water, heat, salt, nutrients, and carbon around the global oceans [Schmittner et al., 2007; Marshall and Speer, 2012]. MOC is calculated using the following equation:

$$
\psi_m(z, \text{lat}) = \int_z^0 \int_{\lambda_W}^{\lambda_E} V \cos(\text{lat}) \, dx \, dz
$$

(2.8)

where $\psi_m$ is the meridional overturning (m$^3$ s$^{-1}$), $z$ is depth (m), $\text{lat}$ is the latitude, $\theta$ is the ocean surface, $\lambda_E$ is maximum longitude east, $\lambda_W$ is maximum longitude west, and $V$ is the ocean velocity in the y direction (m s$^{-1}$). $\psi_m$ is then multiplied by 1x10$^6$ for MOC in Sv.
Figure 2.3: Meridional overturning circulation (MOC, Sv) for a) Ctrl-RSC and b) Ctrl-PDSC. Counterclockwise rotating cells are positive, while clockwise rotating cells are negative.

The MOC is characterized by two relatively shallow, hemispherically symmetric cells centered at about +/- 15° (tropical cells) with a weaker but deeper cell reaching below 2000 m at ~40°N (associated with circumpolar currents). Overall, the Ctrl-RSC has a similar dynamic ocean as the Ctrl-PSDC, despite the differences in SSTs (Figs. 2.2b and Figs. A.1-A.4). The MOC pattern is essentially the same, with counter-rotating cells at the same latitudes, although there are some minor differences in the Southern Hemisphere deep oceans. The magnitude of the values is similar in many spots, although the MOC in Ctrl-RSC is somewhat increased (up to 10 Sv) in some pockets relative to Ctrl-PDSC. We have deemed these minor differences to be acceptable for analysis with the much warmer conditions derived from Ctrl-PDSC, even if these warmer conditions are not necessarily accurate for the Late Ordovician.
Figure 2.4 shows the zonally averaged profile of dissolved oxygen (\(\mu\text{mol L}^{-1}\)) for Ctrl-PDSC and the oxygen concentration at 3200 m. The oxygen profile (Fig. 2.4a) shows much of the anoxia (<10 \(\mu\text{mol L}^{-1}\)) around the tropical oxygen minimum zone, typical of a highly productive area. There is also deep ocean anoxia around the equator and lower values up to 30\(^\circ\)N, but otherwise the deep ocean is well oxygenated. There exists some mid-level depletion of oxygen in northern hemisphere, but not to the point of anoxia. The oxygen concentrations near the ocean bottoms (Fig. 2.4b) show a vast area of anoxic waters on the western coast of Gondwana to the shelf containing Baltica and Siberia around 30\(^\circ\)E and anoxia waters along the mid-ocean ridge west of Laurentia around the equator. The rest of the deep ocean is well oxygenated, most notably in the southern hemisphere, where the majority of the landmasses are located (mainly Gondwana).

Figure 2.5 shows the rate of NPP for Ctrl-PDSC (mol N m\(^{-3}\) yr\(^{-1}\)). For most of the oceans, NPP is very low, but there are locations of enhanced NPP around 30\(^\circ\)N and 30\(^\circ\)S. These regions tend to be related to generally cooler waters (Fig. 2.2b) and potentially upwelling (Fig. 2.3b). Overall, without any enhancement to biogeochemical or nutrient processes in the Ctrl-PDSC simulation, NPP is relatively muted.
Figure 2.4: a) Zonally averaged dissolved oxygen concentrations (μmol L⁻¹) for Ctrl-PDSC and b) dissolved oxygen concentrations at 3200 m. Anoxic regions (<10 μmol L⁻¹) are the deepest reds and outlined by a black dashed line.

Figure 2.5: Rate of surface phytoplankton net primary production (mol N m⁻³ yr⁻¹) for Ctrl-PDSC.
Table 2.2 shows climate diagnostics for each simulation. Our values for the tropical SSTs from all simulations agree with temperature reconstructions for the Katian by Finnegan et al. [2011] and Trotter et al. [2008]. Finnegan et al. [2011] used clumped carbonate isotopes and trace metal concentrations to derive tropical SSTs between ~38°C in the latest Katian to ~29°C in the middle Hirnantian. Trotter et al. [2008] used conodont oxygen isotopes and found temperatures ranging from ~32°C in the early Katian to ~24°C in the middle Hirnantian. Our simulations range from 27.85°C to 34.8°C, which broadly agrees with the above findings. Both Finnegan et al. [2011] and Trotter et al. [2007] concluded that cooling in the Late Katian leading to the Hirnantian glaciation contributed to limited cooling in the tropical oceans. Our simulated air temperature and sea ice extent results agree with these conclusions, particularly for the two coolest simulations (Ctrl-RSC and Min CO$_2$) where air temperatures cooled and sea ice was present, but tropical oceans were still relatively warm.

### Table 2.2: Climate variable diagnostics from each simulation.

<table>
<thead>
<tr>
<th>Diagnositcs</th>
<th>Global Avg. Air Temp</th>
<th>Avg. Tropical SSTs</th>
<th>Sea Ice Extent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Units</td>
<td>°C</td>
<td>°C</td>
<td>km$^2$</td>
</tr>
<tr>
<td>Ctrl-RSC</td>
<td>13.70</td>
<td>27.85</td>
<td>5.95E+06</td>
</tr>
<tr>
<td>Ctrl-PDSC</td>
<td>22.19</td>
<td>34.04</td>
<td>0</td>
</tr>
<tr>
<td>Red CO$_2$</td>
<td>20.31</td>
<td>32.79</td>
<td>0</td>
</tr>
<tr>
<td>Min CO$_2$</td>
<td>16.91</td>
<td>30.64</td>
<td>1.89E+06</td>
</tr>
<tr>
<td>Red O$_2$</td>
<td>21.88</td>
<td>34.80</td>
<td>0</td>
</tr>
<tr>
<td>2xPO$_4$</td>
<td>22.18</td>
<td>34.04</td>
<td>0</td>
</tr>
<tr>
<td>2xNO$_3$</td>
<td>22.18</td>
<td>34.04</td>
<td>0</td>
</tr>
<tr>
<td>2xNO$_3$/PO$_4$</td>
<td>22.17</td>
<td>34.04</td>
<td>0</td>
</tr>
<tr>
<td>Red Wind</td>
<td>21.88</td>
<td>34.80</td>
<td>0</td>
</tr>
<tr>
<td>Ctrl-Flat</td>
<td>21.89</td>
<td>34.30</td>
<td>0</td>
</tr>
</tbody>
</table>
2.4. Results

Below are selected results for the simulations listed in Table 2.1. The remainder of the paper will feature comparisons with the present day solar constant (Ctrl-PDSC) simulation. While we are interested in the role of Ordovician paleogeography and environments on ocean oxygenation, we are also interested in the conditions within the UVic ESCM that favor anoxic conditions. These simulations represent first steps in exploring possible anoxic conditions in the Ordovician, with more Ordovician experiments presented in Chapter 3. The reduced solar constant (Ctrl-RSC) simulation is still discussed in results and discussion.

Figure 2.6 shows a comparison of dissolved oceanic oxygen. The three simulations with the lowest oxygen concentrations compared to Ctrl-PDSC are those with increased nitrate flux (2xNO₃, Fig. 2.6a), reduced atmospheric O₂ (Red O₂, Fig. 2.6b), and the flat bottom (Ctrl-Flat, Fig. 2.6c). Clearly, not all of the experiments in Fig. 2.6 have a major impact on anoxia or oxygen concentrations relative to the Ctrl-PDSC, so further analysis will only feature a select few simulations. The analysis will focus on the experiments showing the most widespread anoxia, with additional consideration for the six potential hypotheses of Late Ordovician anoxia from Melchin et al. [2013].
Figure 2.6: Zonally averaged dissolved oxygen anomalies (μmol L⁻¹) comparing a) Ctrl-PDSC – 2xNO₃, b) Ctrl-PDSC – Red O₂, c) Ctrl-PDSC – Ctrl-Flat, d) Ctrl-PDSC – 2xPO₄, e) Ctrl-PDSC – 2xPO₄/NO₃, f) Ctrl-PDSC – Red Wind, g) Ctrl-PDSC – Red CO₂, h) Ctrl-PDSC – Min CO₂, and i) Ctrl-PDSC – Ctrl-RSC. Positive values (reds) represent regions where the Ctrl-PDSC simulation had higher average values of dissolved oceanic oxygen, while negative values (blues) represent regions where the experimental simulation had higher average values of dissolved oceanic oxygen. The green dot-dash line represents anoxic water (< 10 μmol L⁻¹) for the Ctrl-PDSC, while the black dashed line represents the anoxic waters for each respective experimental simulation. See Table 2.1 for a list of the simulations and abbreviations.
Figure 2.7 contains a comparison of variables for Ctrl-PDSC – 2xNO₃, which had the largest region of bottom anoxia (Figs. 2.6a and 2.7a). The largest region where there is significantly less dissolved oxygen in 2xNO₃ than in Ctrl-PDSC exists in the high latitude Northern Hemisphere, which also contains a wide area of anoxia (Fig. 2.7a). Figure 2.7b shows where a general, but small, increase in NPP for 2xNO₃ relative to Ctrl-PDSC and Fig. 2.7d shows that MOC is very similar for both 2xNO₃ and Ctrl-PDSC, generally within 1 Sv, so these were likely not the causes of the large variations in oxygen concentration. Figure 2.7c shows anomalies in export of detritus (μmol N m⁻³ yr⁻¹) around 1100 m, near the average depth of the thermocline, on top of the anomalies in dissolved oxygen at 3200 m. The negative values show where export of detritus was higher for 2xNO₃ than Ctrl-PDSC. Although the differences in NPP were relatively insignificant for the scales in Fig. 2.7b, detritus nonetheless increased in the column, increasing oxidation and uptake of dissolved oxygen and reducing deep ocean oxygen concentrations.
Figure 2.7: a) Ctrl-PDSC – 2xNO\textsubscript{3} anomalies in dissolved oxygen (\(\mu\text{mol L}^{-1}\)) at 3200 m where warm colors indicate less oxygen for 2xNO\textsubscript{3} and cool colors indicate less oxygen for Ctrl-PDSC. Areas of anoxia (\(O_2 < 10 \mu\text{mol L}^{-1}\)) are also highlighted for 2xNO\textsubscript{3} (black dashed line and diagonal hatching) and Ctrl-PDSC (green dot-dash line and vertical hatching). b) Ctrl-PDSC – 2xNO\textsubscript{3} anomalies in ocean surface net primary production (NPP, mol N m\textsuperscript{-3} yr\textsuperscript{-1}), where cool colors indicate regions of increased NPP for 2xNO\textsubscript{3} and warm colors indicate regions of increased NPP for Ctrl-PDSC. c) Ctrl-PDSC – 2xNO\textsubscript{3} dissolved oxygen anomalies as in a) with anomalies in export of detritus (\(\mu\text{mol N m}^{-3} \text{ yr}^{-1}\)) at 1100 m, where dashed green lines represent regions of increased detrital export for 2xNO\textsubscript{3} and solid purple lines represent regions of increased detrital export for Ctrl-PDSC. d) Ctrl-PDSC – 2xNO\textsubscript{3} anomalies in meridional overturning circulation (MOC, Sv) where warm colors indicate increased MOC for 2xNO\textsubscript{3} and cool colors indicated increased MOC for Ctrl-PDSC.

The simulation with the second largest region of bottom anoxia was Red O\textsubscript{2} (Figs. 2.6b and 2.8a). Figure 2.8a shows the dissolved oxygen at 3200 m and the majority of the oceans feature reduced deep ocean oxygen when atmospheric oxygen is depleted. Figures
2.8b, 2.8c, and 2.8d do not have large anomalies from Ctrl-PDSC and are likely not having a large impact on the deep ocean oxygen. The oxygen in the atmosphere has a direct impact on the oxygen in the oceans, as shown in García and Gordon [1992] and will not have a major impact on ocean dynamics. A reduction in atmospheric oxygen can contribute to anoxic conditions, but anoxic conditions also provide a negative feedback, as increased burial of organic carbon is a source of oxygen to the atmosphere, which can work to reduce anoxic volume. This feedback cannot be represented dynamically in the UVic ESCM at this time, so a long period of reduced atmospheric oxygen will only contribute to the reduction of dissolved oxygen in the water column.
Figure 2.8: As in Fig. 2.7, but for Ctrl-PDSC – Red O$_2$.

The third largest depletion of deep ocean oxygen is seen in the Ctrl-Flat experiment (Figs. 2.6c and 2.9a). A large area of the deep ocean anoxia and the largest anomalies in dissolved oxygen relative to Ctrl-PDSC occur in the high latitude northern hemisphere. Large anomalies are not seen in NPP (Fig. 2.9b) or in the export of detritus (Fig. 2.9c), but the changes in dynamics and MOC are quite large (Fig. 2.9d). Although there is not a very large change in the MOC north of 60°N, we still see decreases in mid-level overturning from 30°N-60°N associated with the disappearance of the northern hemisphere mid-ocean ridge in Ctrl-Flat. A change in the ocean dynamics and a reduction
in the overturning can have major impacts on the dissolved oxygen concentration in the deep oceans.

**Figure 2.9:** As in Figure 2.7, but for Ctrl-PDSC – Ctrl-Flat.

The next three experiments that will be analyzed in this section did not show significant reductions in deep ocean oxygen or increases in anoxia relative to Ctrl-PDSC, but are important biogeochemically (2xPO$_4$) or climatically (Red CO$_2$, Ctrl-RSC). Figures 2.6d and 2.10a show the anomalies in dissolved oxygen for Ctrl-PDSC – 2xPO$_4$. The majority of the ocean contains more dissolved oxygen for Ctrl-PDSC, but we do not see an impact as large as 2xNO$_3$ in the 2xPO$_4$ experiment. Increases in NPP for 2xPO$_4$
are straddling the equator around 10°N and 10°S (Fig. 2.10b), which could be the result of increased phytoplankton mass due to the additional PO₄, but variations are not as strong away from 10°, either poleward or equatorward. Enhanced sinking of detritus is also observable (Fig. 2.10c), which could contribute to the somewhat enhanced anoxia from 10°N-20°N north of the mid-ocean ridge (Fig. 2.10a). Changes in MOC (Fig. 2.10d) are extremely small as expected, and likely have almost no impact on deep ocean oxygen for 2xPO₄.

**Figure 2.10:** As in Fig. 2.7, but for Ctrl-PDSC – 2xPO₄.
The area of anoxia does shrink slightly for RedCO₂ (Figs. 2.6g and 2.11a), but generally speaking, Ctrl-PDSC and RedCO₂ are very similar. The largest enhancement for Red CO₂ relative to Ctrl-PDSC, which is friendly to anoxia, is the large increase in NPP in the Laurentian basin (Fig. 2.11b), but this would not have a major impact on deep ocean anoxia, although it will have an impact on the shallower shelf. Anomalies in detrital export are very small (Fig. 2.11c) and clearly have not impacted Red CO₂ oxygen concentrations in any additional way relative to Ctrl-PDSC. MOC has increased for a majority of the ocean in the cooler climate of Red CO₂ (Fig. 2.11d), and this might have an impact on the higher concentrations of oxygen in the southern hemisphere relative to Ctrl-PDSC.
Figure 2.11: As in Fig. 2.7, but for Ctrl-PDSC – Red CO₂.

The experiment with the least anoxia and the largest portion of the oceans more oxygenated than the Ctrl-PDSC is the Ctrl-RSC (Figs. 2.6i and 2.12a). NPP along the equator is fairly significantly reduced for Ctrl-RSC (Fig. 2.12b) relative to Ctrl-PDSC, which can explain some of the lack of anoxia (Fig. 2.12a). Additionally, Ctrl-PDSC has more export of detritus around the equator (Fig. 2.12c) and globally. As mentioned above, the patterns of MOC are similar for Ctrl-PDSC and Ctrl-RSC (Fig. 2.3), but the magnitudes are different. With cooler conditions, MOC is increased almost everywhere for Ctrl-RSC relative to Ctrl-PDSC (Fig. 2.12d), another feature that would tend to limit deep ocean anoxia through the ventilation of the deep oceans.
2.5. Discussion

2.5.1. Hydrographic setting, sea level, and climate change

The impact of the hydrographic setting, here restricted to ocean bottom shape, on modeled anoxia is apparent in the significant changes between simulations with and without ocean ridges. As can be seen from Ctrl-Flat (Figs. 2.6c and 2.9), a flat ocean bottom results in relatively widespread bottom anoxia in the Northern Hemisphere high latitudes, a feature not present in other experiments. With the exception of Red O$_2$ (Fig. 2.6b) and 2xNO$_3$ (Fig. 2.6a), most of the anoxia for the Ctrl-PDSC and the other
experiments is confined to the tropical oxygen minimum zone, above the thermocline where oxygen has been taken up by respiration and oxidation of detritus. The bathymetry does not appear to enhance conditions for bottom anoxia, but the continental shelves do possess additional anoxia higher in the water column above the actual shelves at 457.5 m depth, particularly in the Laurentian basin and off the northwest coast of Gondwana. Generally speaking, the continental shelves help to create basins that are more nearly enclosed, which tends to favor bottom anoxia in highly productive regions [Melchin et al., 2013]. The average profiles of oxygen do not depict this impact quite as strongly (Fig. 2.6), but it is important to note that “bottom” anoxia does exist at higher levels than those shown in Figs. 2.7-2.12.

Figure 2.13 shows a regional plot of dissolved O₂ for Laurentia at a depth of 457.5 m, just above the continental shelf depth, for the Ctrl-RSC, one of the experiments deemed “least prone to anoxia”, along with the anoxic area for the Ctrl-PDSC and Ctrl-RSC simulations. The presence of the continental shelf in these simulations allows for both to experience anoxia in the semi-isolated Laurentian basin. All of the experiments, in addition to Ctrl-PDSC, have anoxia at 457.5 m in the given basin. Whether this can be linked to the shelves themselves or to the typical oxygen minimum zone requires further investigation.
Figure 2.13: Regional plot of Laurentia showing the dissolved oxygen concentration (μmol L$^{-1}$) for the Ctrl-RSC simulation at 450 m. Overlaid are regions of anoxia (< 10 μmol L$^{-1}$) for Ctrl-PDSC, featuring vertical hatching and enclosed by the green dot-dash line and for Ctrl-RSC, featuring the diagonal hatching and enclosed by the black dashed line.

Changes in sea level and hydrographic settings can all be linked to climatic conditions. In a generally warm and high CO$_2$ time period [Berner, 2006], such as the latest portions of the middle Ordovician or the earlier portions of the Late Ordovician, sea level would be high and conditions would, over time, be more favorable for the development of anoxia. In order to test the climate change hypothesis, the CO$_2$ level was reduced (Red CO$_2$ and Min CO$_2$). It can be seen by the oxygen anomalies of Min CO$_2$ (Fig. 2.6h) and Red CO$_2$ (Figs. 2.6g and 2.11a) that the CO$_2$ concentration in the atmosphere had only marginal impacts on the concentration of dissolved O$_2$ in the deep oceans. CO$_2$ does impact climate in the UVic ESCM, but it has a less direct impact on the
concentration of dissolved oxygen in the deep ocean, although temperature is a variable present in the oxygen saturation equation of García and Gordon [1992] shown in Equation 2.5.

The impact of temperature is clearer when reducing the solar constant (Ctrl-RSC). Regions of anoxic water are smaller, particularly at 3200 m for Ctrl-RSC (Fig. 2.12a) compared to Red CO₂ (Fig. 2.11a). Ctrl-RSC has an increased impact on the overturning (Fig. 2.12d) compared to the Red CO₂ (Fig. 2.11d), being nearly an order of magnitude larger, which helps to ventilate the ocean through enhanced downwelling and eliminates some of the bottom anoxia relative to Ctrl-PDSC and Red CO₂. This makes sense, as reducing the solar constant by nearly 55 W m⁻² reduces the radiation received at Earth by about 14 W m⁻². Reducing CO₂ by a factor of 2 only reduces the radiative forcing by around 3.7 W m⁻² [IPCC, 2013]. In the range of parameters explored by our simulation, the MOC, general circulation, and mixing, and therefore upwelling of nutrients and downwelling of O₂, in the UVic ESCM is impacted more by the winds than the atmospheric CO₂. Overall, climate does have an impact on the presence of anoxia in the UVic ESCM, but its impacts are very small and limited to the continental shelves. Warmer conditions are clearly more favorable to anoxia than cooler conditions, as expected, but the impact of CO₂ was relatively minor in agreement with Misumi and Yamanaka [2008], Montenegro et al. [2011], and Ozaki et al. [2011].

2.5.2. Nutrient input, recycling, and changes to the biosphere

As stated above, increases in primary production at the ocean surface and just below the ocean surface contribute to depletion of dissolved CO₂ and enhancement of
dissolved O$_2$ due to photosynthesis. Figures 2.7b, 2.8b, 2.9b, 2.10b, 2.11b, and 2.12b show the NPP anomalies relative to the Ctrl-PDSC simulation. The anomalies are mainly subdued, with a few notable exceptions. The nearly isolated basin of Laurentia shows a strong signal for the 2xNO$_3$ (Fig. 2.7b), Red O$_2$ (Fig. 2.8b), and Ctrl-Flat (Fig. 2.9b) relative to Ctrl-PDSC with exceptions from Ctrl-RSC (Fig. 2.12b) and 2xPO$_4$ (Fig. 2.10b). As seen in Fig. 2.13, the Laurentian Basin is anoxic near its bottom, even for the anoxia unfriendly Ctrl-RSC. This could be attributed to enhanced NPP, in addition to the region’s bottom being close to the depth of the oxygen minimum zone.

Primary production levels are connected to nutrient concentrations in the oceans. Two experiments featured enhanced nutrient inputs into the oceans – 2xNO$_3$ and 2xPO$_4$ – to test the impact of nutrient loadings on dissolved O$_2$. These nutrients may have increased in the Late Ordovician due to enhanced chemical weathering due to mountain building events, such as the Taconic Orogeny, the spread of non-vascular land plants, or due to warm, moist climatic conditions, such as those during the BWE. Figure 2.7b clearly shows increases in NPP for the 2xNO$_3$ in the tropical oceans, which makes sense, as nitrate is the main limiting nutrient in the present-day oceans, despite the constant presence of N$_2$ in the atmosphere. When PO$_4$ concentrations are high, cyanobacteria have an evolutionary advantage through the ability to fix their own N, so they are able to re-establish the Redfield ratio, making N limiting again. There is also an increase in the area of anoxic waters shown in Figs. 2.6a and 2.7a. Clearly, the simple doubling of N has contributed to enhanced bottom anoxia, particularly away from the equator in the Northern Hemisphere mid and high latitudes.
Figures 2.7d, 2.8d, 2.9d, 2.10d, 2.11d, and 2.12d show the oxygen concentration anomalies along with the anomalies of detrital export near the thermocline. NPP alone cannot explain why there would be a reduction of dissolved O$_2$ in the deep oceans, but the export of detritus near the thermocline should give some proxy of oxygen uptake in the deep oceans. Export of organic matter to deeper layers does not differ significantly from the control in most experiments. The largest exception is 2xNO$_3$ (Fig. 2.7a); a relatively sizeable negative anomaly in exists in detrital export, meaning more export for the experiment, near a large anomaly in the dissolved O$_2$ at 3203.5 m in the sub-polar and high latitude northern hemisphere. This could explain some of the enhanced anoxia associated with 2xNO$_3$ in the Northern Hemisphere, one of two simulations with any bottom anoxia away from the Tropics and subtropics. Subtle changes in NPP due to the increased N concentrations contribute to more export and subsequent oxidation of detritus, taking up dissolved O$_2$ in the water column.

The modeled doubling of phosphate flux (2xPO$_4$) was not effective at increasing NPP (Fig. 2.10b) or area of anoxic waters (Figs. 2.6d and 2.10a). Falkowski [1997] and Saltzman [2005] point out the debates in the oceanographic community regarding the limiting nutrient and in our simulations the addition of P into the oceans does not enhance productivity, the uptake of dissolved O$_2$, or the spread of bottom anoxia because NO$_3$ has a stronger control. It should also be noted that different types of phytoplankton will respond differently to enhancement of NO$_3$ and PO$_4$, so we should not expect the same responses to the different nutrients. In particular, enhancement of PO$_4$ will mainly impact
tropical diazotrophs [Schmittner et al., 2008], and there is a small signal of both enhanced NPP (Fig. 2.10b) and export of detritus (Fig. 2.10c) near the equator for 2xPO$_4$.

In addition to the simple addition and enhancement of nutrient loadings, it has also been theorized that enhanced recycling of nutrients (particularly P) and delivery of nutrients from below the ocean surface can promote the spread of bottom anoxia. This current research has not yet been able to test this hypothesis, but it does remain a topic of interest that will be addressed in future research.

2.5.3. Atmospheric oxygen levels

There exists a clear connection between the ocean and the atmosphere regarding oxygen. As described above and through the equations of García and Gordon [1992], the concentration of oxygen in the atmosphere has a direct impact on dissolved oxygen in the oceans, as the atmosphere is the major source of oxygen gas to the oceans. Figure 2.6b and Figure 2.8a show the immediate impact of the Red O$_2$ experiment, where O$_2$ concentrations in the atmosphere were decreased from 12% to 8% by total atmospheric volume based on estimates by Berner [2006]. Red O$_2$ had the second largest area of bottom anoxia in the zonally averaged dissolved O$_2$ experiments (Fig. 2.6b) and in the O$_2$ concentration near ocean bottom (Fig. 2.8a). Red O$_2$ also had the largest proportion of positive O$_2$ anomalies (higher dissolved O$_2$ concentration in Ctrl-PDSC) in the Southern Hemisphere, although like the other experiments, its southern hemisphere ocean remains largely oxygenated. Clearly, the reduction of oxygen in the atmosphere has a direct and noticeable impact on oxygen in the oceans and is one of the two major contributors, along
with increased nutrient loadings to bottom anoxia in these Late Ordovician simulations of
the UVic ESCM.

2.5.4. Comparison to black shale locations in Melchin et al. [2013]

Late Ordovician bottom anoxia is certainly important, and can be simulated with the
modification of several different variables, but the majority of this paper has only
attempted to simulate total anoxia and less focus has been given to how simulated anoxia
spatial patterns compare to the location of well-preserved black shales. Figure 4 in
Melchin et al. [2013] shows the presence of black shales, interbedded black shales, and
oxic localities during the Late Katian, mid-Hirnantian, and Early Rhuddanian (early
portion of the Silurian, ~440 ma). Although our sea level is higher, our paleogeography is
most similar to that of the Late Katian ([Melchin et al., 2013] Fig. 4a), where we can see
black shales preserved in continental shelves and in deeper shelf sediments. Figure 2.14
shows deep ocean anoxia and continental shelf anoxia (like that shown in Fig. 2.13) for
the experiments covered in Section 2.3 of this paper. With the exceptions of 2xNO₃ and
Ctrl-Flat (Figs. 2.14b and 2.14d), deep ocean anoxia (3200 m) exists mainly on the west
coasts of Gondwana and Laurentia. Well-preserved black shales do exist off the western
continental shelf of Laurentia in Fig. 4a of [Melchin et al., 2013], but data is much more
limited in deep oceans beyond these non-shelf points.
Figure 2.14: Anoxia (dissolved oxygen concentration < 10 µmol L⁻¹) at 450 m (vertical hatching outlined by green dot-dash line) and at 3200 m (diagonal hatching outlined by black dashed line) for a) Ctrl-PDSC, b) 2xNO₃, c) Red O₂, d) Ctrl-Flat, e) 2xPO₄, f) Red CO₂, and g) Ctrl-RSC.
Most of the black shales exist on the continental shelf (Fig. 4a in *Melchin et al.* [2013]). Figure 2.14 shows relatively expansive anoxia just above the continental shelf (450 m), particularly on the western coast of North Gondwana, the western coast of Laurentia, and within the Laurentian basin for all experiments. This agrees well with locations of Late Katian black shales (Fig. 4a from *Melchin et al.* [2013]), in addition to the few well preserved mid-Hirnantian black shales (Fig. 4b from *Melchin et al.* [2013]) during peak glaciation. The southern hemisphere in Fig. 4a from *Melchin et al.* [2013] is entirely either oxic or dysoxic, which is also reproduced well in our experiments (Fig. 2.14).

Despite the many sources of uncertainty associated with our experiments, our results reproduce the locations of black shales well for the Late Katian in deep waters and on the continental shelves. Our results do not approach the levels of anoxia for the Early Rhuddanian, where there was potentially a very large influx of freshwater into the oceans from melting Hirnantian glaciers, so perhaps more modeling study of the early Silurian would benefit our understanding of Late Ordovician kill mechanisms.

2.6. Chapter 2 Conclusions

Simulations of the varying climatic, oceanic, and biogeochemical conditions in the Late Ordovician using the UVic ESCM were conducted to evaluate a select set of impacts on deep ocean oxygenation. *Melchin et al.* [2013] covered six potential scenarios that may have contributed to the anoxia in the Late Ordovician and also covered the larger event in the early Silurian that may have been caused by a large influx of freshwater from melting Hirnantian glaciers. Through this modeling effort, the apparent
causes for bottom anoxia in the Late Ordovician were primarily linked to low concentrations of O$_2$ in the atmosphere or to additional inputs of nutrients in the oceans, particularly NO$_3$.

Prior research had proposed that widespread bottom anoxia is unlikely without some modification to NPP by increasing the concentration or cycling of nutrients [Meyer et al., 2008; Misumi and Yamanaka, 2008; Montenegro et al., 2011; Ozaki et al., 2011] or slowing the settling rates of detrital particles [Butterfield 2009]. It appears that simulations using the UVic ESCM with a Late Ordovician paleogeography and bottom topography will not favor deep ocean anoxia simply by changes to radiative forcing alone (i.e., modifying the concentration of CO$_2$ in the atmosphere or the solar output), although some regions with well-preserved black shales have been reproduced on the continental shelves.

In the next chapters, this initial research of Ordovician oceanic oxygen will serve as the foundation for additional experiments. Our next sets of simulations will test various other processes that may have impacted oxygen in the Late Ordovician oceans, including the reduction of detrital settling rates [Butterfield, 2009], the darkening of the oceans [Butterfield, 2009], and the enhancement of nutrient remineralization [Van Capellen and Ingall, 1994; Slomp and Van Cappellen, 2007]. We are also interested in the causes of the Early Silurian anoxia and the input of glacial melt on deep ocean oxygenation [Melchin et al., 2013].

Today, anthropogenic climate change is warming and acidifying our oceans. Several hypoxic or anoxic dead zones already exist in regions where rivers input large
amounts of nutrients into the oceans. These UVic ESCM simulations of the Late Ordovician agree with the current observations of our present day planet. Warming oceans alone are not enough to cause expansion of anoxia, but combined with changes in biogeochemical cycling and productivity, the future for marine life – particularly when combined with overfishing and bycatch – potentially could face negative consequences as human impacts increase on our planet.
Chapter 3. Simulating deep ocean oxygen in the Late Ordovician with an Earth system climate model: Impacts of organic matter remineralization, settling velocities, and ocean surface albedo

3.1. Chapter 3 Introduction

Environmental changes in the Late Ordovician (458-444 Ma) were rapid and remarkable. The period is noted for a mass extinction event [Melchin et al., 2013; Harper et al., 2014; Sheets et al., 2016], which impacted an estimated 85% of marine animal species and 25% of animal families, a brief episode of widespread glaciation during the Hirnantian (445-444 Ma). Although it is now widely recognized that the glaciation, with a reduced scope, likely began earlier in the Ordovician and continued well into the Silurian (444-419 Ma) [Trotter et al., 2008, 2016; Finnegan et al., 2011] This time interval was also characterized by periods of potentially widespread deep ocean anoxia [Armstrong et al. 2009a; Hammarlund et al., 2012; Jones and Fike, 2012; Thompson and Kah, 2012; Melchin et al., 2013].

The events in the Early (485-470 Ma) and Middle Ordovician (470-458 Ma) set the stage for extreme changes in the Late Ordovician. Atmospheric CO₂ concentrations were high during the Ordovician, with a range that might have spanned from 4x the pre-industrial atmospheric levels (PAL, here defined as 280 ppmv) to 18xPAL [Herrmann et al., 2004b; Berner, 2006; Pohl et al., 2014]. The Early Ordovician began with an increase

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in biodiversity known as the Great Ordovician Biodiversity Event (GOBE), featuring a significant proliferation in the biodiversity of marine benthic organisms and phytoplankton, as well as the development of a diverse zooplankton assemblage [Servais et al., 2010]. Along with the increase of oceanic diversity, the first evidence of non-vascular land plants appeared during the Middle Ordovician [Vecoli et al., 2011; Lenton et al., 2012; Porada et al., 2016].

Given high concentrations of CO$_2$, the first appearances of land plants, and potentially, the young rocks associated with the Taconic Orogeny, rates of chemical weathering were likely quite high. Coupled with the warm temperatures of the Boda Warming Event (447-445 Ma) [Armstrong et al., 2009b; Fortey and Cocks, 2005], oceanic primary production was likely high due to the increased nutrient inputs. This may have contributed to instances of large-scale ocean bottom anoxia in pre-Hirnantian marine sediments [Melchin et al., 2013]. As chemical weathering and the expansion of land plants continued, atmospheric CO$_2$ was taken up and cooling commenced prior to the Hirnantian age [Cherns and Wheeley, 2007; Lenton et al., 2012; Porada et al., 2016], contributing to the onset of the glaciation event. The environmental changes prior to the Hirnantian and the glaciation during the Hirnantian likely both contributed to the first wave of mass extinction, where planktic and particularly benthic species became extinct [Melchin et al., 2013; Harper et al., 2014; Sheets et al., 2016].

Following the Hirnantian glacial interval, euxinia and anoxia may have developed once again or expanded as sea levels began to rise, killing off many of the survivors of the first wave of extinction [Melchin et al., 2013]. Both phases of mass extinction can be
potentially linked to ocean bottom anoxia and the glaciation event, as both events would have shifted habitable zones for certain species, forcing either mass marine migration or extinction. \textit{Rorhssen et al.} [2013] and \textit{Melchin et al.} [2013] also suggested linkages between the extinction events and the communities of bacterial and algal primary producers; around the time of the extinction events, nitrogen isotopes suggest primary production was reliant on nitrogen fixed by cyanobacteria \cite{LaPorte et al., 2009}, a smaller phytoplankton, which are susceptible to very low settling rates \cite{Butterfield, 2009}. The two waves of extinction in the Late Ordovician disrupted the GOBE and contributed to a plateau in biodiversification until the Permian-Triassic extinction event (~252 Ma) \cite{Harper et al., 2014}.

Physical evidence for anoxia existed from many locations, mainly in the form of organic-rich black shales in Late Ordovician and the earliest Silurian (444 Ma) \cite{Armstrong et al., 2009a; Berry, 2010; Thompson and Kah, 2012; Melchin et al., 2013}. Although the stratigraphic evidence suggests that oceanic anoxia was more restricted in marine shelf and slope environments during the Hirnantian glacial interval \cite{Melchin et al., 2013}, there is controversy surrounding the extent of anoxia in the bathyal and abyssal parts of the oceans during the peak in glaciation \cite{Hammarlund et al., 2012; Melchin et al., 2013; Jones and Fike, 2013}.

\textit{Melchin et al.} [2013] discussed six potential causes for anoxia leading up to and during the Late Ordovician: 1) hydrographical setting of the marine basin; 2) changes in sea level and climate; 3) rate of nutrient input into the oceans; 4) rate of nutrient recycling within the oceans; 5) atmospheric oxygen levels; and 6) changes in the biosphere.
Melchin et al. [2013] also argued that the six factors are necessarily speculative, as there have been no attempts to model these conditions using numerical models. D’Amico et al. [under revision, submitted to Paleoceanography, Chapter 2 of this dissertation] (hereafter referred to as D17) addressed some of these six hypotheses using the University of Victoria Earth System Climate Model (UVic ESCM) [Weaver et al., 2001]. Specifically, D17 examined the impacts of atmospheric CO2, atmospheric O2, bathymetry, winds, and increases of the nutrients PO4 and NO3 into the oceans.

The aim of this research is to expand on the work of D17 with the UVic ESCM. For a more complete overview on Late Ordovician climate modeling and modeling of deep ocean anoxia, refer to D17 or Chapter 2 of this dissertation. Here we will focus on simulating three potential impacts on deep ocean oxygen that were not covered in the D17 study. The first is the remineralization of phosphorus, whereby enhanced burial of organic carbon under anoxic conditions contributes to enhanced organic phosphorus regeneration, which might lead to increases in primary production and further reduction in ocean oxygen concentrations [Ingall et al., 1993; Ingall and Jahnke, 1994; Lenton and Watson, 2000a]. The caveat in this situation is that increased burial of organic carbon is a source of atmospheric oxygen [Lenton and Watson, 2000a, b; Saltzman 2005], which tends to counteract the anoxic conditions that lead to this enhanced organic carbon burial.

Experiments were also conducted to simulate the impact of increased ocean stratification on the biological pump O2 distribution. Butterfield [2009] discussed a set of potential oceanic states that could impact mid- to deep-ocean oxygen levels and how oxygen impacts the evolution of animals. Reduction in atmospheric levels of oxygen is a
point of discussion, but the author suggested that this cannot have exclusive control on evolution or deep ocean anoxia events. Variations in the biological pump have been shown to contribute to the uptake of oxygen in the oceans below the oxygen minimum zone (OMZ). Butterfield [2009] examined two stable states of the marine biological pump. The state similar to a majority of the present day ocean is dominated by relatively large eukaryotic phytoplankton, which sink quickly, contributing to a well-mixed clear-water system, with ample oceanic ventilation. This situation would favor oxic conditions below the oxygen minimum zone. The state that may have contributed to the relatively large-scale ocean anoxia events in the Paleozoic (~540-250 Ma) and Mesozoic (~250-66 Ma) may have been associated with smaller cyanobacteria-dominated phytoplankton, which would settle to the ocean bottom more slowly, increasing respiration and oxygen consumption in the water column. This contributes to a stratified, turbid water column with limited ventilation [Butterfield, 2009].

A third set of simulations involves the darkening of the oceans by reducing ocean surface albedo. A situation like this could occur in an ocean, as proposed by Butterfield [2009], dominated by smaller, slow sinking cyanobacteria. The higher absorption of shortwave radiation near the surface, associated with a reduction in sub-surface shortwave absorption would warm the surface, cool the subsurface, increase vertical stratification and reduce ventilation [Butterfield, 2009; Winguth and Winguth 2012].

This study aims to add to the work of D17 by testing the impacts on oceanic O₂ of enhanced remineralization, reduction in the settling speed of particles, specifically detritus, and reduction in the ocean albedo. The next section will outline the methods.
used for the various experiments. The third section will feature results, followed by discussion, and the final section contains concluding thoughts.

3.2. Methods

This study utilizes the UVic ESCM Version 2.9, a model of intermediate complexity. A more complete description of the UVic ESCM and its components can be found in Weaver et al. [2001], Schmittner et al. [2005], and Schmittner et al. [2008], as well as D17. As in D17, the winds and paleogeographies are derived from Herrmann et al. [2003; 2004a, b] and are completely available in D'Amico et al. [2017]. To our knowledge, the paleogeographic reconstructions of more recent Late Ordovician climate modeling studies, such as Pohl et al. [2016a] and Porada et al. [2016], could not be utilized in this study, as the wind fields for their given paleogeographies have not been published but are required boundary conditions for the UVic ESCM. The paleogeography, ocean bathymetry, and wind stress vectors can be found in Fig. 3.1, with a more complete description of each in D17.
Figure 3.1: Bathymetry (m, contours) and wind stress vectors (white arrows) utilized in each experimental and control simulation.

The solar constant will follow that typically used in Late Ordovician climate modeling studies [Endal and Sofia, 1981; Crowley and Baum, 1995; Herrmann et al., 2004a], around 1313 W m$^{-2}$, a value around 96% of the present day solar constant. Orbital parameters were kept at present day values. One level of atmospheric CO$_2$ was utilized, 12xPAL (3360 ppmv), which fits in well with CO$_2$ ranges for other modeling studies in the Late Ordovician [Herrmann et al., 2004a, b; Pohl et al., 2014, 2016a, b; Porada et al., 2016] and within the range of geochemical models [Berner, 2006]. In D17, the authors tested the impact of CO$_2$ on deep ocean oxygen, but varied CO$_2$ concentrations did not have a major impact on deep ocean oxygen on their own.
Experiments with remineralization, settling rates, and albedo were conducted under two levels of atmospheric oxygen, 12% by volume and 8% by volume. Changes in model atmospheric O$_2$ concentrations were implemented in the same way as in D17 using the equations of Garcia and Gordon [1992].

The next sections will detail the specific changes to remineralization rates, particle settling velocities, and ocean albedo, followed by a list of all of the experiments that will be discussed in this study.

3.2.1. Remineralization rates

In the model, organic detritus is remineralized in the water column through the following relationship:

$$\mu_D = \mu_{D_0} \exp \left( \frac{T}{T_B} \right) [0.65 + 0.35 \tanh(O_2 - 6)]$$

(3.1)

where $\mu_D$ is the remineralization of detritus, $\mu_{D_0}$ is the initial remineralization rate ($0.048$ day$^{-1}$), $T$ is the water temperature in $^\circ$C, $T_B$ is the e-folding temperature of biological rates ($15.65^\circ$C), and $O_2$ is the concentration of dissolved oxygen in $\mu$mol.

Here, we tested a simple increase in remineralization rate prior to anoxic conditions, to see if we could mimic the positive feedback between remineralization and deep ocean oxygen consumption. In order to do so, we multiplied a present day value of remineralization ($0.048$ day$^{-1}$) by $1.5$ ($0.072$ day$^{-1}$). This number was chosen somewhat arbitrarily, as, to our knowledge, there are few studies that examine remineralization values under anoxic conditions. Additionally, alterations to the UVic ESCM need to be done with care, as the model can become numerically unstable, providing no useable
model output, when changes are either sudden or very large, particularly for paleoclimate studies.

3.2.2. Settling velocities of detritus

There are multiple ways to test the Butterfield [2009] hypotheses. One is to reduce the particle size of phytoplankton and zooplankton. We are currently investigating the steps necessary to do this and plan on utilizing this approach in future work. The second involves reducing the fall velocities of particles. We have done this for detritus, slowing the sinking speed from 6.0 m day$^{-1}$ to 3.0 m day$^{-1}$. The value selected for particle velocity was again, somewhat arbitrary, as little evidence exists on the actual settling velocities necessary to redesign the biological pump in favor of anoxia. The third feasible option involves darkening the oceans to mimic the turbidity of a cyanobacterially-dominated biological pump. This process will be explained in the next section.

3.2.3. Reduction of ocean albedo

We increased the ocean surface coalbedo (1 – albedo, or the fraction of radiation that is absorbed) in order to test the impact of increased turbidity and darkened oceans on deep ocean oxygen. The original ocean surface coalbedo in the UVic ESCM is as follows:

$$\alpha_0 = 0.87 + 0.02 \cos|\varphi|$$

(3.2)

where $\alpha_0$ is the ocean surface coalbedo (unitless) and $\varphi$ is the latitude in radians. This equation decreases the albedo from the equator to the poles, which is intended to represent the presently observed latitudinal distribution of albedo. In order to reduce the albedo, we increased the leading constant to:
\[ \alpha_0 = 0.96 + 0.02 \cos|\varphi| \]  

so that we can reduce the entire ocean’s albedo. While this might be somewhat unrealistic, given a lack of knowledge on the spatial distribution of primary production by cyanobacteria at the period, we deemed this to be the least arbitrary way to implement the change. Additionally, we aim to test the extremes in regard to ocean oxygenation, so albedo levels are pushed to the brink of numerical stability with the UVic ESCM. As the goal of these experiments was to test the influence of surface ocean albedo on stratification and not its impacts of global energy budget and climate, the darkening of the ocean is accompanied by increase in land surface albedo from an average desert value of 0.3 to an average ice value around 0.6. This is a necessary step, as we are assuming no vegetation on our land surface, so all non-ice covered portions of the planet have the same surface albedo. This actual surface albedo value will also vary with latitude [Weaver et al., 2001]. Although this is a more extreme change, Figure 3.1 clearly demonstrates that the majority of our paleogeography dataset is ocean, contributing more surface overall to albedo than the land.

Figure 3.2 also shows anomalies of net radiation (incoming – outgoing) at the top of the atmosphere (TOA, W m\(^{-2}\)) and surface air temperatures (°C) between the two albedo (abbreviated LoO2-Alb and HiO2-Alb) experiments and the two control experiments (abbreviated LoO2-Ctrl and Hio2-Ctrl), where the control experiment is subtracted from the albedo experiment with the same O\(_2\) concentration. In examining the net TOA radiation (Figs. 3.2a and 3.2c), there is clearly a large deficit (more radiation exiting than entering for the albedo experiments relative to the control) over the land.
surface, while anomalies over the oceans are generally relatively smaller, despite the large decrease in albedo. Air temperatures (Figs. 3.2b and 3.2d) respond to the large deficit in radiation above the land surface by cooling slightly and only where the landmasses are large (i.e., central Gondwana). The oceans remain warmer due to decreased albedo and have a strong influence on the smaller continents. No change between Figs. 3.2a and 3.2c, and Figs. 3.2b and 3.2d indicated that atmospheric oxygenation has no impact on air temperatures or TOA radiation.
Figure 3.2: a) Net radiation (W m$^{-2}$) at the top of the atmosphere (TOA) for LoO2-Alb – LoO2-Ctrl, where positive values (warm colors) represent more incoming radiation than outgoing radiation TOA for LoO2-Alb relative to LoO2-Ctrl. b) Surface air temperature (°C) for LoO2-Alb – LoO2-Ctrl, where positive values (warm colors) represent regions that are warmer for LoO2-Alb relative to LoO2-Ctrl. c) As in a), but for HiO2-Alb – HiO2-Ctrl. d) As in b), but for HiO2-Alb – HiO2-Ctrl. Additional information on abbreviations can be found in Table 3.1 below.

With reduced albedo, we also expect increased stratification. Figure 3.3 shows the first derivative of potential density of the reduced albedo and control simulations with higher oxygen concentration to a depth of around 1200 m for a global average of potential density (Fig. 3.3a, kg m$^{-3}$), a tropical average potential density (Fig. 3.3b), a Northern Hemisphere high latitude average potential density (Fig. 3.3c), and a Southern Hemisphere high latitude potential density (Fig. 3.3d). Lowering albedo caused a general
increase in near surface stratification, with the largest differences found in the Northern Hemisphere high latitudes (Fig. 3.3c).

Figure 3.3: First derivative of potential density \([10^{-3} \text{(kg m}^{-4})]\) with depth for a) globally averaged potential density (kg m\(^{-3}\)), b) tropical (20\(^\circ\)S to 20\(^\circ\)N) averaged potential density, c) Northern Hemisphere high latitude (66\(^\circ\)N to 90\(^\circ\)N) potential density, and d) Southern Hemisphere high latitude (90\(^\circ\)S to 66\(^\circ\)S) potential density. HiO2-Ctrl (red curve) and HiO2-Alb (black curve) are plotted on each graph to \(~1200\) m depth. See Table 3.1 for an explanation on simulation abbreviations.
3.2.4. Experiments

Table 3.1 below shows all of the features of the experiments for this study. The two control simulations (LoO2-Ctrl and HiO2-Ctrl) begin from initial conditions, i.e., they are given the standard paleogeography, winds, and \( \text{O}_2 \) concentrations and run for around 6000 years, so that ocean kinetic energy, ocean potential temperature, and oceanic oxygen are stable. All experimental simulations are initiated using the climate state of the stable high and low atmospheric oxygen control simulations as initial conditions, and are modified as listed. Using the same criteria as the control experiments, the remineralization (Remin) and settling velocity (SetVel) simulations stabilized after 4000-6000 years. The albedo (Alb) simulations took longer to become stable, about 10,000 years, because the coalbedo had to be increased in small increments.

Table 3.1: List of experimental simulations utilized for this research. Abbreviations and shorthands are as follows: LoO2 = low oxygen concentration; HiO2 = high oxygen concentration; Ctrl = control; Alb = reduced oceanic albedo; Remin = enhanced remineralization rates; SetVel = reduced settling velocities of detritus; \( \varphi \) = latitude in radians.

<table>
<thead>
<tr>
<th>Simulation</th>
<th>( \text{O}_2 ) Conc Units</th>
<th>Remin Rate ( \text{day}^{-1} )</th>
<th>Set Velocity ( \text{m day}^{-1} )</th>
<th>Ocean Coalbedo Unitless</th>
</tr>
</thead>
<tbody>
<tr>
<td>LoO2-Ctrl</td>
<td>8 % by Volume</td>
<td>0.048</td>
<td>6</td>
<td>( 0.87 + 0.02 \cos(\varphi) )</td>
</tr>
<tr>
<td>HiO2-Ctrl</td>
<td>12</td>
<td>0.048</td>
<td>6</td>
<td>( 0.87 + 0.02 \cos(\varphi) )</td>
</tr>
<tr>
<td>LoO2-Alb</td>
<td>8</td>
<td>0.048</td>
<td>6</td>
<td>( 0.96 + 0.02 \cos(\varphi) )</td>
</tr>
<tr>
<td>LoO2-Remin</td>
<td>8</td>
<td>0.072</td>
<td>6</td>
<td>( 0.87 + 0.02 \cos(\varphi) )</td>
</tr>
<tr>
<td>LoO2-SetVel</td>
<td>8</td>
<td>0.048</td>
<td>3</td>
<td>( 0.87 + 0.02 \cos(\varphi) )</td>
</tr>
<tr>
<td>HiO2-Alb</td>
<td>12</td>
<td>0.048</td>
<td>6</td>
<td>( 0.96 + 0.02 \cos(\varphi) )</td>
</tr>
<tr>
<td>HiO2-Remin</td>
<td>12</td>
<td>0.072</td>
<td>6</td>
<td>( 0.87 + 0.02 \cos(\varphi) )</td>
</tr>
<tr>
<td>HiO2-Setvel</td>
<td>12</td>
<td>0.048</td>
<td>3</td>
<td>( 0.87 + 0.02 \cos(\varphi) )</td>
</tr>
</tbody>
</table>
Time averages of variables are saved every 20 years and there is a restart file produced every 100 years for the entire life of each simulation. All UVic ESCM simulations for this research were run on the Oakley cluster at the Ohio Supercomputer Center [OSC, 2012]. All post-processing was done using the NCAR Command Language version 6.2.1 [NCL, 2014].

3.3. Results

3.3.1. Experimental simulations minus control simulations

Figure 3.4 shows the zonally averaged anomalies (experimental simulation minus the control simulation for each atmospheric oxygen level) in dissolved ocean oxygen ($\mu$mol L$^{-1}$). The largest negative anomalies in oxygen (less oxygen in the experimental simulation than in the control simulation) are seen in LoO2-Alb – LoO2-Ctrl (Fig. 3.4a) and in HiO2-Alb – HiO2-Ctrl (Fig. 3.4d) and these two decreased albedo simulations also contain the largest areas of anoxia, mainly in the mid-oceans, but also feature some expansion of anoxia into the deep oceans. Generally speaking, the remaining experimental simulations do not seem to have a major impact on the spread of anoxia, with generally positive oxygen anomalies, particularly in the Northern Hemisphere deep oceans (Figs. 3.4b, 3.4c, 3.4e, and 3.4f) where some anomalies are approaching +60 $\mu$mol L$^{-1}$. 
Figure 3.4: Zonally averaged dissolved oxygen profiles (µmol L$^{-1}$) and anoxia (dissolved O$_2$ < 10 µmol L$^{-1}$) for a) LoO2-Alb – LoO2-Ctrl, b) LoO2-Remin – LoO2-Ctrl, c) LoO2-SetVel – LoO2-Ctrl, d) HiO2-Alb – HiO2-Ctrl, e) HiO2-Remin – HiO2-Ctrl, and f) HiO2-SetVel – HiO2-Ctrl. Positive values (cool colors) represent regions where the experimental simulation had higher dissolved oxygen concentrations than the control simulation and negative values (warm colors) represent regions where the experimental simulation had lower dissolved oxygen concentrations than the control simulation. The black dashed lines represent regions of anoxia for the experimental simulations, while the green dot-dash line represents regions of anoxia for the control simulation. See Table 3.1 for complete list of abbreviations.

Figure 3.5 contains a comparison for variables for LoO2-Alb – LoO2-Ctrl. Figure 3.5a shows the anomalies in dissolved oxygen at 3200 m, near the ocean bottom, but with a large portion of the ocean still above the depth of the mid-ocean ridges. The largest negative oxygen anomalies exist in the southern hemisphere and the anoxia is relatively
widespread, at least on par with the LoO2-Ctrl simulation (Fig. 3.5a). Figure 3.5b shows anomalies in sea surface temperatures (SSTs). As expected, the reduction in ocean albedo has had a major impact on SSTs, with the entire LoO2-Alb ocean featuring higher temperatures. The warmer ocean temperatures contribute to a decrease in deep-ocean overturning, particularly in the Southern Hemisphere, as shown in Fig. 3.5g. Anomalies in net primary production (NPP) are shown in Fig. 3.5c. The majority of the ocean shows more NPP for LoO2-Alb, particularly in the tropics. Even though NPP is increased, there is no marked difference in surface NO$_3$ concentration (Fig. 3.5d) and a slight reduction in surface PO$_4$ concentration (Fig. 3.5e). Enhanced NPP also contributes to enhanced particle sinking ($\mu$mol N L$^{-1}$ yr$^{-1}$) at a depth of 1100 m (near the thermocline) in the tropics, as shown in Fig. 3.5f. This may have contributed to somewhat enhanced uptake of oxygen, but does little to explain the expansion of anoxia away from the tropics, which, in the albedo experiments, are related to a decrease in deep overturning.
Figure 3.5: a) Anomalies in dissolved oxygen (µmol L\(^{-1}\)) for LoO2-Alb – LoO2-Ctrl at 3200 m depth, where negative values (warm colors) represent regions where LoO2-Alb had a lower dissolved oxygen concentration than LoO2-Ctrl. Areas of anoxia (O\(_2\) < 10 µmol L\(^{-1}\)) are also outlined for LoO2-Alb (black dashed line and diagonal hatching) and LoO2-Ctrl (green dot-dash line and horizontal hatching). b) LoO2-Alb – LoO2-Ctrl anomalies in sea surface temperatures (SSTs, °C), where positive values (warm colors) represent higher SSTs for LoO2-Alb relative to LoO2-Ctrl. c) LoO2-Alb – LoO2-Ctrl anomalies in ocean surface net primary production (NPP, mol N m\(^{-3}\) yr\(^{-1}\)) where positive values (cool colors) represent regions of increased NPP for LoO2-Alb relative to LoO2-Ctrl. d) LoO2-Alb – LoO2-Ctrl anomalies in ocean surface NO\(_3\) concentrations (µmol L\(^{-1}\)) where positive values (warm colors) represent regions of increased NO\(_3\) for LoO2-Alb relative to LoO2-Ctrl. e) LoO2-Alb – LoO2-Ctrl anomalies in ocean surface PO\(_4\) concentrations (µmol L\(^{-1}\)) where positive values (warm colors) represent regions of increased PO\(_4\) for LoO2-Alb relative to LoO2-Ctrl. f) LoO2-Alb – LoO2-Ctrl anomalies in export of detritus (µmol N L\(^{-1}\) yr\(^{-1}\)) at 1100 m where positive values (warm colors) represent areas of enhanced sinking for LoO2-Alb relative to LoO2-Ctrl. g) LoO2-Alb – LoO2-Ctrl anomalies in meridional overturning circulation (MOC, Sv) where negative values (warm colors) represent regions of decreased MOC for LoO2-Alb relative to LoO2-Ctrl.
Figure 3.6 shows the comparison of the same variables as Fig. 3.5, but for HiO2-Alb – HiO2-Ctrl. The dissolved oxygen anomalies at 3200 m are largely positive (Fig. 3.6a), but due to the higher concentration of oxygen in the atmosphere, the extent of bottom anoxia is reduced in both the experimental and control simulations. Despite the overall reduction in anoxia, HiO2-Alb still has a large pocket of bottom anoxia off the west coasts of Gondwana and Laurentia, locations with well-preserved Late Ordovician aged black shales [Melchin et al., 2013]. Anomalies in SSTs are entirely positive (Fig. 3.6b) due to the reduction in albedo, and this has contributed to some slowing of deep-ocean overturning (Fig. 3.6g) in the Southern Hemisphere. Fig. 3.6c shows the anomalies in NPP, showing enhanced production in the tropical oceans for HiO2-Alb, but the NO$_3$ concentrations (Fig. 3.6d) and PO$_4$ concentrations (Fig. 3.6e) would not favor this trend in NPP, as was the case for LoO2-Alb – LoO2-Ctrl. The slight enhancement of NPP again leads to more particle sinking near the thermocline (Fig. 3.6f).

Figures 3.7 and 3.8 show comparisons of selected variables for LoO2-Remin – LoO2-Ctrl and HiO2-Remin – HiO2-Ctrl, respectively. Oxygen anomalies are completely negative for both sets of comparisons, and neither experimental simulation with remineralization features any bottom anoxia (Figs. 3.7a and 3.8a). Figures 3.7b and 3.8b show anomalies in NPP for the two comparisons and both LoO2-Remin and HiO2-Remin feature subtle increases in NPP in the tropical oceans, less than the LoO2-Alb and HiO2-Alb, and this has not directly translated to the formation of bottom anoxia. Figures 3.7c and 3.8c show the anomalies in PO$_4$ concentration, and the majority of the oceans for both LoO2-Remin and HiO2-Remin, the warm oceans in particular, show an increased
concentration of PO$_4$. This means that the 1.5x enhancement of remineralization is working correctly and more PO$_4$ is being delivered to the ocean surface, but the additional PO$_4$ is not contributing to enhanced NPP or the formation of deep ocean anoxia. Figures 3.7d and 3.8d show the sinking of detritus near the thermocline, and indicate a general decrease for the remineralization experiment relative to the control experiment. This means less organic material is being exported from the surface oceans to the deep oceans, which by decreasing respiration and oxygen consumption below the thermocline, results in higher O$_2$ levels in the deeper layers.
Figure 3.6: As in Fig. 3.5, but for HiO2-Alb – HiO2-Ctrl.
Figure 3.7: a) Anomalies in dissolved oxygen (µmol L⁻¹) for LoO2-Remin – LoO2-Ctrl at 3200 m depth, where positive values (cool colors) represent regions where LoO2-Remin had a higher dissolved oxygen concentration than LoO2-Ctrl. Areas of anoxia (O₂ < 10 µmol L⁻¹) are also outlined for LoO2-Ctrl (green dot-dash line and horizontal hatching). b) LoO2-Remin – LoO2-Ctrl anomalies in ocean surface net primary production (NPP, mol N m⁻³ yr⁻¹) where positive values (cool colors) represent regions of increased NPP for LoO2-Remin relative to LoO2-Ctrl. c) LoO2-Alb – LoO2-Ctrl anomalies in ocean surface PO₄ concentrations (µmol L⁻¹) where positive values (warm colors) represent regions of increased PO₄ for LoO2-Remin relative to LoO2-Ctrl. d) LoO2-Remin – LoO2-Ctrl anomalies in export of detritus (µmol N L⁻¹ yr⁻¹) at 1100 m where positive values (warm colors) represent areas of enhanced sinking for LoO2-Remin relative to LoO2-Ctrl.
Figures 3.9 and 3.10 show comparisons of selected variables for LoO2-SetVel – LoO2-Ctrl and HiO2-SetVel – HiO2-Ctrl, respectively. Ocean bottom oxygen anomalies are again mostly negative, and there is no presence of deep ocean anoxia (Figs. 3.9a and 3.10a), with the exception of a small area off of the western coast of Gondwana. Again, both LoO2-SetVel and HiO2-SetVel feature subtle increases in NPP for the majority of the oceans relative to the control simulations (Figs. 3.9b and 3.10b), but this was not enough to favor development of bottom anoxia. Figures 3.9c and 3.10c show the export of detritus at 1100 m depth. The anomaly values are almost entirely negative, showing that particles are indeed sinking more slowly, but this results in more remineralization.
near the surface, less organic matter available for respiration below the thermocline and higher oxygen concentrations in the deep ocean.

Figure 3.9: a) Anomalies in dissolved oxygen (µmol L⁻¹) for LoO2-SetVel – LoO2-Ctrl at 3200 m depth, where positive values (cool colors) represent regions where LoO2-SetVel had a higher dissolved oxygen concentration than LoO2-Ctrl. Areas of anoxia (O₂ < 10 µmol L⁻¹) are also outlined for LoO2-Ctrl (green dot-dash line and horizontal hatching) and LoO2-SetVel (black dashed line and diagonal hatching). b) LoO2-SetVel – LoO2-Ctrl anomalies in ocean surface net primary production (NPP, mol N m⁻³ yr⁻¹) where positive values (cool colors) represent regions of increased NPP for LoO2-SetVel relative to LoO2-Ctrl. c) LoO2-SetVel – LoO2-Ctrl anomalies in export of detritus (µmol N m⁻³ yr⁻¹) at 1100 m, where positive values (warm colors) represent areas of enhanced sinking for LoO2-SetVel relative to LoO2-Ctrl.
3.3.2. Anoxia on the continental shelf

Although this study aims to address deep ocean anoxia in the Late Ordovician, anoxia on the continental shelf could have been a large contributor to benthic extinctions following the peak of the Hirnantian glaciation in late Hirnantian time. Figure 3.11 shows anoxic areas in the 300-450 m and 2775-3200 m layers for all 8 basic simulations. Each simulation featured more anoxia at 450 m than at 3200 m, but this is not a surprising result, given that 450 m can easily be a depth within the typical oceanic oxygen minimum zone. The control and reduced albedo simulations featured the most anoxia, both on the continental shelf and in the deep ocean. All simulations feature some anoxia in the 450 m
depth, including in tropical locations west of Gondwana, west of Laurentia, within the
Laurentian Basin, and in the ocean between Laurentia, Baltica, and Avalonia.
Figure 3.11: Anoxia (dissolved oxygen concentration < 10 μmol L⁻¹) at 450 m (vertical hatching outlined by green dot-dash line) and at 3200 m (diagonal hatching outlined by black dashed line) for a) LoO2-Ctrl, b) HiO2-Ctrl, c) LoO2-Alb, d) HiO2-Alb, e) LoO2-Remin, f) HiO2-Remin, g) LoO2-SetVel, and h) HiO2-SetVel.
3.4. Discussion

3.4.1. Remineralization

Remineralization of phosphorus tends to occur in anoxic oceans and can be an additional source of PO$_4$ to enhance surface NPP and further deplete O$_2$ concentrations, creating a positive feedback [Ingall et al., 1993; Ingall and Jahnke, 1994; Lenton and Watson, 2000a]. In experiments with a simple enhancement of detrital remineralization, we do see an increased concentration of PO$_4$ at the surface (Figs. 3.7c and 3.8c), but the increases in NPP are marginal at best (Figs. 3.7b and 3.8b) and confined completely to the tropics. Without vast changes to the biological pump and enhanced primary productivity, the formation of anoxia is completely controlled by climate, ocean dynamics, and ocean thermodynamics. Several modeling studies have found that changes in climate and ocean dynamics are not sufficient to spread deep ocean anoxia into a large-scale event [Misumi and Yamanaka, 2008; Montenegro et al., 2011; Ozaki et al., 2011; Monteiro et al., 2012; D17].

This also raises questions about how the UVic ESCM treats the concentration of macronutrients in relation to phytoplankton NPP. As described in D17, the calculation of NPP is complex function of chlorophyll content, light supply, and temperature [Schmittner et al., 2008]. The ocean productivity dynamics in the UVic ESCM are based on present day conditions, where the limiting nutrient is, despite some debate in the oceanography community, generally believed to be NO$_3$ [Falkowski, 1997]. This means the addition of PO$_4$ by remineralization might not have a large enough impact to enhance NPP and the spread of anoxia. PO$_4$ tends to impact tropical diazotrophs [Schmittner et al.,
and our results show enhanced NPP in the tropics, but this did not cause a significant change in the uptake of dissolved $O_2$ in the deep oceans. The ecosystem model in the UVic ESCM is based on Redfield stoichiometry, so it is likely that remineralization is saturating the surface ocean with PO$_4$ and NO$_3$ is becoming even more limiting. As NO$_3$ becomes more limited, one would expect increased diazotroph population, particularly those that can fix their own nitrogen (i.e., cyanobacteria), which are slow growing and able to outcompete the faster growing phytoplankton [Schmittner et al., 2007b]. This indicates that the UVic ESCM oceans, even in paleoclimate simulations, are limited by NO$_3$ and not PO$_4$. The supply of N$_2$ in the atmosphere is unlimited, so as long as N fixation can occur in the present day mimicking oceans [Lenton and Watson, 2000a], increases in PO$_4$ concentrations will not have strong impacts on NPP seen with increases in NO$_3$ [D17].

The higher remineralization rate resulted in a nearly global increase in deep of deep ocean $O_2$. One potential factor for the increased dissolved $O_2$ could be related to where detritus is being remineralized. When the remineralization rate is increased, there is a decreased in export of detritus out of the surface oceans into the deep oceans (Figs. 3.7d and 3.8d). This indicates that remineralization is being accelerated in the surface oceans, and fewer detrital particles are actually entering the deep ocean and being oxidized than in the control simulations. Given this, it would be interesting to test modifications to remineralization below the thermocline, where biological uptake of nutrients is sparse, to test if we still have the same response in PO$_4$ and NPP at the
surface and oxygen in the deeper oceans. This is outside of the scope of the current research.

3.4.2. Ocean stratification and particle sinking

As climate warms and the ocean circulation becomes more sluggish, it has been suggested that cyanobacterially-dominated picoplankton might have an evolutionary advantage [Butterfield, 2009]. These smaller sized particles may have had an immense impact on the biological pump, partially through their very slow settling velocities. Slow settling velocities and smaller particle sizes lead to water column turbidity and enhanced oxidation of particles as they slowly sink. Experiments where the initial detrital settling velocities were decreased do show a reduction in particle settling near the thermocline (Figs. 3.9c and 3.10c), but do not contribute to the development or spread of deep ocean anoxia in the UVic ESCM simulations. Large portions of the oceans actually attain higher dissolved O2 concentrations with reduced initial particle settling velocities (Figs. 3.9a and 3.10a). According to Schmittner et al. [2005; 2008], in the UVic ESCM the sinking of detritus does have an impact on NPP through nutrient trapping, which is increased with slower particle velocities. We do see a slight increase in NPP in our experiments (Figs. 3.9b and 3.10b), but again, this has not translated into the spread of anoxia.

What might be more important to the depletion of oxygen in the water column is the oxidation of sinking particles [Butterfield, 2009]. Figures 3.9c and 3.10c show fewer particles reaching the thermocline, which is indicative of both the speed that they fall and where they are remineralized. As mentioned above, the increase in remineralization accelerated nutrient cycling near the surface, reduced organic matter arriving below the
thermocline, and resulted in higher deep ocean oxygen concentrations. If there were a method to only reduce settling velocities in the deep ocean, this might prove to be a more useful exercise in the context of Butterfield [2009], but to our knowledge, that is something not readily available in the UVic ESCM or in other current ocean models. This would deviate from the Butterfield [2009] hypothesis slightly, because smaller plankton would always originate near the surface and would likely fall slowly through the entire depth. Additionally, we could try to slow remineralization rates and see if slowing down particles without fast recycling and remineralization leads to additional uptake of oceanic oxygen.

3.4.3. Darkening of the oceans

Present day oceans, which are largely dominated by relatively large eukaryotic plankton with relatively fast settling velocities, are generally well-mixed, clearer, and more reflective. Increased stratification, sluggish overturning circulation and smaller particle sizes can lead to more turbid (darker) ocean waters and reduced albedo [Butterfield, 2009]. Experiments with a global reduction in ocean albedo show a reduction in ocean total oxygen and a slight expansion of anoxia relative to the control experiments (Figs. 3.4a, 3.4d, 3.5a, and 3.6a). The reduction in albedo clearly contributed to increased SSTs (Figs. 3.5b and 3.6b) and a reduction in deep-ocean overturning (Figs. 3.5f and 3.6f), which could have contributed to the initial development of anoxia. This is the first point where climate warming could be argued as a somewhat larger contributor to the development of anoxia and the overall reduction of dissolved oxygen, particularly in the Southern Hemisphere where there is a sharp reduction in deep ocean oxygen (Figs.
3.4a and 3.4d) and presence of anoxia (Figs. 3.11c and 3.11d) associated with a reduction in deep MOC (Figs. 3.5g and 3.6g). The warm water and increased stratification likely produced somewhat of a positive feedback; less oxygen to begin with due to lower O$_2$ saturation, more respiration, and remineralization at the surface coupled with reduced communication between the surface and deep oceans further reduces oxygen concentrations in the mid-depth oceans particularly in the Northern Hemisphere high latitudes, where we see the largest increase in near-surface stratification (Fig. 3.3c).

The albedo experiments are also noteworthy due to the enhancement of NPP (Figs. 3.5c and 3.6c). The majority of the increased NPP occurs in the tropics, and associated with an increase in NO$_3$ (Figs. 3.5d and 3.6d) and general decreases in PO$_4$ (Figs. 3.5e and 3.6e). Generally speaking, increasing SSTs would contribute to general reductions in NPP [Gregg et al., 2003], with the exception of the tropics, where a minor increase is noted. Our experiments do agree with increased NPP in the tropics, but do not agree with reduced NPP in the mid- to high-latitudes, unlike as shown in Gregg et al. [2003]. As NPP increased, sinking of detritus increased, which could contribute to additional uptake of oxygen below the thermocline, but only in the tropics. With the LoO2-Alb – LoO2-Ctrl, the deep ocean anoxia expanded away from the tropics (Figs. 3.5a and 3.6a), and was caused by a reduction in overturning and not the sinking of detritus (Figs. 3.5f and 3.6f).

3.4.4. Comparison to black shale locations in Melchin et al. [2013]

Despite a lack of deep ocean anoxia for most of the experiments, it is still worthwhile to compare simulated regions of anoxia with the actual locations of Late
Ordovician aged black shales. Figure 4 in Melchin et al. [2013] shows the locations of black shales prior to the Hirnantian, during the Hirnantian glaciation, and in the early Rhuddanian (early Silurian, ~440 ma). The paleogeography we use is most similar to the pre-Hirnantian paleogeography of Melchin et al. [2013] (their Fig. 4a). Some black shales do exist in the Late Ordovician deep sediments, but a majority exist on the continental shelves, particularly on the western shelves of Gondwana and Laurentia. Figure 3.11 contains anoxia for both control simulations and all 6 experimental simulations at 450 m depth and 3200 m depth. Although the remineralization and settling velocity experiments have generally increased oxygen concentrations across the entire depth of the oceans, every simulation features anoxia at 450 m depth (just above the height of the continental shelves in Figure 3.1) in the tropics. The shelves off of the west coasts of both Gondwana and Laurentia are anoxic, with the widest expanses coming from the LoO2 simulations (Figs. 3.11a, 3.11c, 3.11e, and 3.11g) and the albedo experiments (Figs. 3.11c and 3.11d), in addition to HiO2-Ctrl (Fig. 3.11b).

This shows us that the paleogeography of the Late Ordovician likely played a role in the development and expansion of anoxia on the continental shelves, but some questions still remain. D17 point out that some of the continental shelf anoxia could be associated with the oxygen minimum zone, which is present around the 450 m depth (generally between 200-1000 m), so some debate still exists. Regardless of the degree of reduction, reduced dissolved oxygen concentrations should still contribute to enhanced burial of organic material and subsequent formation of organic rich black shales, so our simulations still match observations of the Late Ordovician fairly well.
3.4.5. Ordovician ocean oxygenation conceptualized

Figure 3.12 shows a process diagram linking experiments in Chapter 2 with those presented here in Chapter 3 and their impacts on ocean oxygenation in the UVic ESCM, for both the deep and the surface oceans. See the caption of Fig. 3.12 for a complete description of what the varying shapes, colors, and lines represent. All of the components present on the diagram can either be modified in the UVic ESCM code or will respond to changes in other variables and impact oxygenation. While this diagram is complete, it is important to note that magnitudes of changes have major impacts and are not represented on this diagram. For instance, in examining “Surface Layer O\textsubscript{2}”, a positive arrow originates from “NPP” and a negative arrow originates from “[Surface Ocean] Remineralization”, but “NPP” has a positive connection to “[Surface Ocean] Remineralization” (Fig. 3.12). Magnitudes of the individual contributors to the receiving variable are important to both the sign and magnitude of the receiving variable being modified.
**Figure 3.12:** Process diagram linking modeled changes in variables to ocean oxygen in the University of Victoria Earth System Climate Model (UVic ESCM). Solid lines without arrows separate the Atmosphere, Surface Ocean, and Deep Oceans. Red rectangular boxes are atmospheric gases. Turquoise ovals are variables and processes present in the surface oceans above the thermocline. Royal blue ovals are variables and processes in the deep oceans below the thermocline. The oval for meridional overturning circulation (MOC) is green because it is the main dynamic feature linking the surface oceans and deep oceans. Arrows represent what happens to the receiving variable when the variable of origin *increases*. Solid arrows indicate that the receiving variable would also increase (i.e., increased atmospheric “O₂” would increase “Surface Layer O₂”). Dashed arrows indicate that the receiving variable would decrease as the variable of origin is increased (i.e., increased “SSTs” would decrease “Surface Layer O₂”). Dotted arrows indicate processes that are not simulated evenly across the globe and represent varying regional changes, which are not well captured in the global UVic ESCM.
Figure 3.12

Atmosphere

- $O_2$
- $CO_2$
- SSTs
- $PO_4$
- $NO_3$
- NPP
- Albedo
- Stratification
- Surface Layer $O_2$
- Remineralization
- Detrital Export

Surface Ocean

Deep Ocean

- Remineralization
- MOC
- Deep $O_2$
3.5. Chapter 3 Conclusions

UVic ESCM simulations featuring Late Ordovician paleogeography and modifications to certain variables are performed to gain additional insight on possible spread of deep ocean anoxia during the time period. Melchin et al. [2013] outlined 6 potential causes for deep ocean anoxia in the Late Ordovician and D17 explored some of those causes, using the UVic ESCM as well. Here, we address additional potential causes for Ordovician anoxia including enhanced remineralization, reduced particle sinking velocities, and reduced ocean surface albedo. The largest contributor to the spread of bottom anoxia is a reduction in surface albedo, while the changes to remineralization and settling velocities actually made the deep oceans more oxic.

While albedo has played a small role in the spread of anoxia in these experiments, the role of atmospheric oxygen is still very large. Anoxia on the continental shelf was more expansive with the lower atmospheric oxygen concentration and the only deep ocean anoxia from the remineralization and settling velocity simulations came from the LoO2-SetVel simulation. Several modeling efforts addressing the spread of deep ocean anoxia concluded that biological or biogeochemical changes were necessary in order to attain widespread anoxia [Misumi and Yamanaka, 2008; Montenegro et al., 2011; Ozaki et al., 2011; Monteiro et al., 2012; D17]. This research broadly agrees with these conclusions, despite remineralization not aiding in the development or spread of anoxia, which could partially be related to the depth of remineralization in our experiments (Fig. 3.12). The more interesting candidate is ocean surface albedo. The impacts of albedo now need to be tested in conjunction with enhancement of nutrients or changes to
biogeochemical cycles to determine whether the spread of anoxia is tied to climatic factors (increased temperatures and slower overturning) or biological factors (increased NPP in the tropics, further export of detritus into the deep oceans).

Regardless, the Ordovician remains a time period of great intrigue to paleoclimatologists, paleoceanographers, paleontologists, and anyone interested in environmental change due to the rapid and widespread environmental changes that occurred during the time period. Perhaps the rapid change in the Ordovician can broaden our understanding of the very rapid anthropogenic changes that Earth is experiencing now. While it is extremely difficult to draw parallels between potential future events and large events in the geologic record, expanding our knowledge of Earth processes through modeling of the past can provide subtle hints about the future of the Earth’s oceans, atmosphere, and biosphere.
Chapter 4. Examining deep ocean oxygen in a changing world: Simulations using an Earth system climate model

4.1. Chapter 4 Introduction

The importance of oxygen to the evolution of life on the planet cannot be understated. As oxygen concentrations in the atmosphere evolved through time, life became more complex and more tolerant of, and reliant on, the highly reactive gas. While the evolution of oxygen is obviously apparent to land-dwelling organisms, the oceans are not an exception, as O$_2$ is a critical constraint on marine ecosystems. If dissolved oxygen levels in the oceans were to decrease, habitats for organisms that require aerobic respiration will become restricted, leading to mortality and dead zones in ocean waters. As the oceans warm due to anthropogenic global warming, regions of diminished O$_2$ concentration will expand through decreased solubility of oxygen in ocean waters [García and Gordon, 1992; Bopp et al., 2002; Matear and Hurst, 2003; Schmittner et al., 2008; Deutsch et al., 2011], as higher water temperatures are less favorable for the dissolution of all gases into ocean waters.

Although dissolution of atmospheric oxygen is indeed important to the spread and development of hypoxia (levels of dissolved oxygen that are lethal for $\sim$50% of marine benthic animals [Deutsch et al., 2011], generally $\sim$60 $\mu$mol L$^{-1}$), or anoxia (lethal for

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~90% of marine benthic animals, < 10 μmol L⁻¹) large scale hypoxic-anoxic events have occurred in the geologic past while the atmosphere was well oxygenated, potentially at levels above present day [Butterfield 2009]. Generally speaking, the causes of hypoxia-anoxia events in a well-oxygenated atmosphere have been linked to either stagnant ocean circulation by generally warming temperatures [Sarmiento et al., 1988; Butterfield, 2009], eutrophication of ocean waters [Diaz, 2001], enhanced delivery of PO₄ to the surface oceans by remineralization [Van Cappellen and Ingall, 1994; Tsandev and Slomp, 2009], changes in the biogeochemical cycling [Misumi and Yamanaka, 2008; Montenegro et al. 2011; Ozaki et al., 2011] or some combination of the four [Melchin et al., 2013; D’Amico et al., under revision].

The exploration of hypoxia-anoxia (and euxinia – anoxia with excess levels of hydrogen sulfide) events of the past have continued using various geological and modeling studies, and study of the future of oceanic oxygen has also increased. Bopp et al. [2002] investigated ocean-atmosphere oxygen fluxes from 1860-2100 using a fully coupled atmosphere-ocean general circulation model (AOGCM) that includes the carbon cycle as described in Dufresne et al. [2002], with an IPCC SRES98-A2 emissions scenario. The main purpose of their investigation was testing the oxygen fluxes from the ocean back into the atmosphere, but parallel to O₂ outgassing is depletion of O₂ within the oceans. Bopp et al. [2002] concluded that outgassing is generally caused by changes in surface water solubility due to rising temperatures, changes in biological production and the carbon cycle, and changes in ocean circulation. Although oxygen concentration in the deep ocean was not quantified, the authors do note that stratification and decreased
formation of deep and intermediate waters is the major contributor of outgassing, due to decreased ventilation of deep and intermediate waters.

*Matear and Hirst* [2003] utilized the Commonwealth Scientific and Industrial Research Organization climate model [*Gordon and O’Farrell, 1997; Hirst et al., 2000*] with a low-order oceanic biogeochemical model [*Matear and Hirst, 1999*] to investigate the long-term climate impacts on ocean oxygenation. The authors utilized the IS92a radiative forcing scenario [*Houghton et al., 1995*] from year 1880 through 2083, and thereafter held radiative forcing constant for 650 years. *Matear and Hirst* [2003] found that oxygen levels diminish in the upper 1.5 km of the global ocean during the first several centuries but approach equilibrium thereafter. This initial decrease was likely related to decreased oxygen solubility in warmer oceans and increased stratification. The deep oceans showed progressive decline in oxygen concentrations for the duration of the simulation by about 30%, largely due to stagnant overturning and limited ventilation, but no anoxia [*Matear and Hirst, 2003*]. The authors did mention that approaching anoxia on a basin wide scale would be a gradual process, but the North Pacific Ocean could have reached anoxia within 1500 years of the end of their simulation period.

*Schmittner et al.* [2008] briefly explored oxygen in a study testing their improved ecosystem model from year 2000 to year 4000 with a business-as-usual A2 emissions scenario [*Nakicenovic et al., 2000*]. The authors concluded that oxygen concentrations would decrease and volume of suboxic water (anoxic, in their study < 5 μmol L\(^{-1}\)) increases, but suboxic zones tend to be too large due to low model resolution and high meridional viscosities, so delivery of oxygen to the Eastern Equatorial Pacific is too
small. The oxygen concentration reaches a low point around the year 2500 and then slowly returns to original levels around the year 3000 as the overturning circulation recovers [Schmittner et al., 2008]. Volume of suboxic water nearly triples by 2500 and remains constant, despite the slow recovery in deep ocean oxygen.

The study of Yamamoto et al. [2015] examined deep ocean oxygen on multimillenial scales. These authors use Model for Interdisciplinary Research on Climate AOGCM [K-1 model developers, 2004] along with an offline biogeochemical model. The authors doubled and quadrupled CO$_2$ levels (from 285 ppmv) after 70 and 140 years, respectively, for 2000 total years of integration to investigate oxygen reduction with long-term global warming. Global deep ocean oxygen was reduced ~10% in the first 500 years with larger reductions in dissolved oxygen for individual ocean basins, particularly in the North Atlantic. Like Schmittner et al. [2008], oxygen begins to recover for Yamamoto et al. [2015] after 500 years and starts to increase above simulated present day values after 600 or 800 years (depending on the CO$_2$ scenario). This was generally caused by a recovery and increase in the formation of Antarctic Bottom Water, which slowly ventilates the deep ocean once again. Yamamoto et al. [2015] attributed the depletion of oxygen to solubility changes, changes in biology, and changes in ocean dynamics, with the largest contributors to O$_2$ depletion being solubility and dynamics and the largest contributors to recovery and overshoot being biology and dynamics.

This research aims to examine the role of climate change, like the above modeling studies of deep ocean oxygen, while expanding them to include the hypotheses of Butterfield [2009] and Mouw et al. [2016], which generally state that a turbid, stratified
water column dominated by slow-sinking cyanobacteria would increase the uptake of dissolved oxygen, leading to a hypoxic-anoxic water column. Several studies have pointed to warming oceans having reduced nutrient and chlorophyll concentrations, which both favor the development of smaller and more low-nutrient tolerant cyanobacteria [Behrenfield et al., 2006; Polovina et al., 2008; Steinacher et al., 2010; Rousseaux and Gregg, 2015; Mouw et al., 2016; Mousing et al., 2017]. This section again utilized the University of Victoria Earth System Climate Model (UVic ESCM) [Weaver et al., 2001] with various levels of CO₂ forcing and modifications to the water column to examine the impacts on deep and intermediate ocean dissolved oxygen. The next section will feature an overview of our methods and modifications to the model and introduce the various experiments. The third section will outline results, the fourth section will feature discussion of the results, and the final section will feature concluding thoughts.

4.2. Methods

4.2.1. Physical ocean and atmosphere

This study utilized the UVic ESCM version 2.9, a model of intermediate complexity [Weaver et al., 2001]. The ocean component is the Geophysical Fluid Dynamics Laboratory (GFDL) Modular Ocean Model (MOM) version 2.2 [Pacanowski, 1995], which is based on the Navier Stokes equations subject to the Boussinesq and hydrostatic approximations. This three-dimensional ocean general circulation model (OGCM) is capable of representing horizontal ocean gyre transport and deep convection processes, which are fundamental for the MOC and O₂ distribution. The GFDL MOM within the UVic ESCM has a spatial resolution of 3.6° longitude by 1.8° latitude, with 19
vertical levels to a depth of 6000 m. Ocean surface temperatures initialize at 26.8°C near the equator, decreasing polewards to values around 15°C at 40°N/S and -1.4°C near the poles (85°N/S). Subsurface temperatures decrease with depth to a value of 1.2°C almost everywhere except the poles, which are colder. Salinity initiates with a global surface range of 33-35‰ except in the northern hemisphere high latitudes, where melt water from Greenland decreases the value to around 31.4‰, which will have an impact on the Atlantic Meridional Overturning Circulation. Subsurface initial values of salinity stabilize around 34.7‰.

Coupled to the full OGCM is a thermodynamic/dynamic sea ice model [Hibler, 1979; Hunke and Dukowicz, 1997; Bitz et al., 2001], allowing for atmosphere-ocean-sea ice coupling. The sea ice model has the ability to represent sea ice dynamics with various options for sea ice thermodynamics and thickness distribution. The ocean component is coupled to a two dimensional (vertically averaged) energy-moisture balance model (EMBM) [Fanning and Weaver, 1996]. Atmospheric heat and water transports are parameterized through advection and Fickian diffusion. Precipitation is assumed to occur when relative humidity exceeds 85% [Weaver et al., 2001]. The EMBM also features parameterizations of radiative transfer including longwave feedbacks from water vapor and CO₂. Because atmospheric dynamics are not explicitly resolved, winds need to be prescribed. Winds are based on the monthly mean data from the National Center for Environmental Prediction-National Center for Atmospheric Research (NCAR) reanalysis project [Kalnay et al., 1996]. Wind stress and geography are shown in Fig. 4.1. Land-atmosphere energy and mass fluxes are calculated by the United Kingdom Met Office
(UKMET) Surface Exchange Scheme land surface model [Best et al., 2011; Clark et al., 2011]. Vegetation dynamics and fluxes are based on Clark et al. [2011].

Figure 4.1: Bathymetry (m, contours) and wind stress vectors (Pa, white arrows over the oceans) for all simulations in this study.

4.2.2. Ocean ecosystem model

Ocean ecosystem processes are simulated by an NPZD (nutrient, phytoplankton, zooplankton, detritus) model [Schmittner et al. 2008], which features a full representation of the carbon cycle. Phosphate (PO$_4$) and nitrate (NO$_3$) are the featured nutrients. Initial surface concentrations of PO$_4$ are around 0.3 μmol L$^{-1}$ at the equator, gradually increasing to a 2 μmol L$^{-1}$ peak around Antarctica and 1.1 μmol L$^{-1}$ around the North Pole. Subsurface concentrations of PO$_4$ below the photic zone have global values around 2
\[ \mu \text{mol L}^{-1} \]. Initial concentrations of NO\textsubscript{3} exhibit a similar pattern, but with surface values of 1.7 \( \mu \text{mol L}^{-1} \) around the equator decreasing to a minimum in each hemisphere (0.4 \( \mu \text{mol L}^{-1} \) at 18\(^\circ\)S and 1.1 \( \mu \text{mol L}^{-1} \) at 53\(^\circ\)N) and then increasing to a peak of 20 \( \mu \text{mol L}^{-1} \) near the poles. Subsurface values are between 31-35 \( \mu \text{mol L}^{-1} \). Tracers include O\textsubscript{2}, dissolved inorganic carbon (DIC), and alkalinity [Schmittner et al., 2008]. Dissolved surface O\textsubscript{2} begins with an initial value of 210 \( \mu \text{mol L}^{-1} \) near the equator, increasing to 350 \( \mu \text{mol L}^{-1} \) near the North Pole and 380 \( \mu \text{mol L}^{-1} \) near Antarctica. Subsurface values below 1000 m show a similar initial pattern as the surface, with 160 \( \mu \text{mol L}^{-1} \) near the equator, increasing to 300 \( \mu \text{mol L}^{-1} \) near the North Pole and 220 \( \mu \text{mol L}^{-1} \) near Antarctica. Inorganic tracers and the nutrients PO\textsubscript{4} and NO\textsubscript{3} are connected by changes in inorganic nutrients and calcium carbonate. DIC and alkalinity are controlled in the marine carbon cycle model by changes in inorganic nutrients and calcium carbonate.

4.2.3. Radiative forcing

Orbital parameters and the solar constant are both maintained at the present day values for the entirety of each simulation. The UVic ESCM also includes forcing from the greenhouse gases water vapor and CO\textsubscript{2}. Water vapor forcing is a component of the EMBM and will change as the EMBM adjusts atmospheric moisture levels [Fanning and Weaver, 1996; Weaver et al., 2001]. Three methods of CO\textsubscript{2} forcing were tested: two constant and one dynamic. The first was a control level based on a pre-industrial value of 280 ppmv. The second level holds CO\textsubscript{2} at a value near the 2016/2017 values: 400 ppmv. The final set tested CO\textsubscript{2} concentrations in a business-as-usual climate change scenario, where the concentrations starting around the 2015 value rise in fashion similar to the A2
scenario [Nakicenovic et al., 2000] for 200 years. This approach led to atmospheric CO$_2$
concentrations at year 2200 of ~1050 ppmv, similar to the maximum values registered in
previous experiments with UVic ESCM which attempted to simulate the consequences of
the complete utilization of all presently available fossil fuels where 5000 Pg of carbon are
emitted into the atmosphere over a 300-year period (~1200 ppmv) [Montenegro et al.,
2007; Eby et al., 2009].

4.2.4. Modifications to the phytoplankton community

One of the hypotheses posed by Butterfield [2009] and Mouw et al. [2016]
regarding hypoxia-anoxia is a change in the current biological pump, whereby large,
prokaryotic phytoplankton with relatively high sinking rates leading to a clear, well
oxygenated water column is shifted to a water column dominated by smaller and slower
settling cyanobacteria, leading to a more turbid, stratified, and oxygen poor water
column. In experiments that attempt to reproduce this scenario, we made 3 modifications:
1) the initial settling velocity of detritus was decreased from 6.0 m day$^{-1}$ to 3.0 m day$^{-1}$.
This will only impact the initial settling from the surface. 2) In order to greater impact the
whole water column, we also slowed the total settling velocity, given in the model by:

$$w_d = \frac{(w_{do}+4\times10^{12})(z_k)}{t_{day}/dz_k}$$  \hspace{1cm} (4.1)

where $w_d$ is the settling velocity of detritus (m day$^{-1}$), $w_{do}$ is the initial settling speed of
detritus (set to 3.0 m day$^{-1}$), $z_k$ is the depth from the surface down to the center of level $k$
(m), $t_{day}$ is the length of one day (86400 s), and $dz_k$ is the depth of the grid box (m). This
equation was multiplied by 0.5, to further slow the sinking velocity of detritus. 3) The
albedo of the surface waters was decreased. In the model, the surface’s coalbedo (fraction of radiation absorbed) is determined by:

$$\alpha_0 = 0.87 + 0.02 \cos|\varphi|$$  \hspace{1cm} (4.2)

where $\alpha_0$ is the coalbedo (unitless) and $\varphi$ is the latitude in radians. This creates a latitudinal gradient of shortwave energy absorption across the oceans. Here, we increase the leading constant to 0.92, which decreases the albedo of the oceans, as a result of higher turbidity.

No adjustment was made to land surface albedo because of the dynamic vegetation cover. In the future, we would like to better quantify the actual role of plankton and chlorophyll concentrations in reducing surface albedo, but this initial first step serves the purpose well.

4.2.5. Experiments

Table 4.1 shows a list of all UVic ESCM control and experimental simulations and modifications made to each one. All simulations feature a cold start, where modifications are made to the model code and then started from initial conditions and run continuously for 200 years. The cold start was used in the interest of time, but Weaver et al. [2001] argued that there are some merits to a cold start that do not necessarily diminish their merits in relation to a “lukewarm” or hot start, where the atmosphere, land surface, and ocean are given more time to spin up before analysis. Cold start simulations begin in radiative equilibrium with their time period, whereas a lukewarm start has a warming commitment [Keen and Murphy, 1997] and has not yet reached radiative
equilibrium, meaning that even after spinup, there will still be a slight temperature deficit relative to expected values.

Table 4.1: List of experimental simulations utilized for this research. Abbreviations and shorthands as follows: Conc = concentration; Init = initial; Set Vel = detritus settling velocity; Ctrl = control; B = change to biological pump (phytoplankton community, both albedo and settling velocity); Alb = reduction to albedo only; Setl = reduction to settling velocity only; DYN = dynamic (time changing) CO$_2$ concentration.

<table>
<thead>
<tr>
<th>Simulation</th>
<th>CO$_2$ Conc</th>
<th>Init Set Vel</th>
<th>Set Vel (Eq. 1)</th>
<th>Ocean Coalbedo (Eq. 2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ctrl-280co2</td>
<td>280 ppmv</td>
<td>6 m day$^{-1}$</td>
<td>Standard</td>
<td>Unitless</td>
</tr>
<tr>
<td>280co2-B</td>
<td>280 ppmv</td>
<td>3 m day$^{-1}$</td>
<td>Reduced</td>
<td>Enhanced</td>
</tr>
<tr>
<td>280co2-Alb</td>
<td>280 ppmv</td>
<td>6 m day$^{-1}$</td>
<td>Standard</td>
<td>Enhanced</td>
</tr>
<tr>
<td>280co2-Setl</td>
<td>280 ppmv</td>
<td>3 m day$^{-1}$</td>
<td>Reduced</td>
<td>Standard</td>
</tr>
<tr>
<td>400co2</td>
<td>400 ppmv</td>
<td>6 m day$^{-1}$</td>
<td>Standard</td>
<td>Standard</td>
</tr>
<tr>
<td>400co2-B</td>
<td>400 ppmv</td>
<td>3 m day$^{-1}$</td>
<td>Reduced</td>
<td>Enhanced</td>
</tr>
<tr>
<td>DYNco2</td>
<td>Dynamic</td>
<td>6 m day$^{-1}$</td>
<td>Standard</td>
<td>Standard</td>
</tr>
<tr>
<td>DYNco2-B</td>
<td>Dynamic</td>
<td>3 m day$^{-1}$</td>
<td>Reduced</td>
<td>Enhanced</td>
</tr>
<tr>
<td>DYNco2-Alb</td>
<td>Dynamic</td>
<td>6 m day$^{-1}$</td>
<td>Standard</td>
<td>Enhanced</td>
</tr>
<tr>
<td>DYNco2-Setl</td>
<td>Dynamic</td>
<td>3 m day$^{-1}$</td>
<td>Reduced</td>
<td>Enhanced</td>
</tr>
</tbody>
</table>

As in the last chapter, time averages of variables are saved every 20 years for the entire duration of each simulation. All UVic ESCM simulations for this research were run on the Oakley cluster at the Ohio Supercomputer Center [OSC, 2012]. All post-processing was done using the NCAR Command Language version 6.2.1 [NCL, 2014].

4.3. Results

4.3.1. Global average dissolved oxygen

Figure 4.2 shows the evolution of atmospheric CO$_2$ concentration (ppmv), sea surface temperatures ($^\circ$C), and oceanic oxygen through time for all six simulations. Each
of their average O$_2$ values begins around 176 $\mu$mol L$^{-1}$ and then their evolution separates rapidly. Oxygen concentrations in simulations only forced by changes to atmospheric CO$_2$ (400co2 and DYNco2) increase slightly for the first 40 years and then begin to fall (Fig. 4.2c). While some change is recorded, O$_2$ concentrations in the control (Ctrl-280co2), remain relatively constant. The 400co2 and DYNco2 both show a more rapid decrease in oxygen, with each one reaching values of 170 $\mu$mol L$^{-1}$ and 162 $\mu$mol L$^{-1}$, respectively, at 200 years. At the end of the 21st century O$_2$ concentration for DYNco2 is ~ 163 $\mu$mol L$^{-1}$. The pattern for both of these simulations shows no sign of stabilizing after year 2200.

Oxygen concentrations for the three simulations with the altered phytoplankton community (280co2-B, 400co2-B, DYNco2-B) rise continuously for the entire period. 280co2-B increases the most rapidly to a value over 190 $\mu$mol L$^{-1}$ while 400co2-B rises to a value of 185 $\mu$mol L$^{-1}$ at 200 years. The DYNco2-B has an almost non-changing slope after the initial increase (from year 0 to around year 20) and finishes the 200 years at around 180 $\mu$mol L$^{-1}$. Clearly, the reduction in detrital falling velocity or the reduction of albedo impacted the concentration of global oxygen, largely increasing the values. The individual albedo simulations (280co2-Alb and DYNco2-Alb) feature the largest decreases in global dissolved oxygen, with the DYNco2-Alb falling to 154 $\mu$mol L$^{-1}$ after 200 years. 280co2-Setl increases O$_2$ concentrations at the fastest rate of any simulation, finishing around 206 $\mu$mol L$^{-1}$, while 280co2-Alb features the second largest reduction in O$_2$, behind DYNco2-Alb, showing the strong impact of albedo on dissolved oxygen.
Figure 4.2: Globally averaged a) atmospheric CO$_2$ concentration (ppmv) for the DYNco2 experiments, b) sea surface temperatures (SSTs, °C), and c) dissolved oxygen in the oceans (μmol L$^{-1}$) for each simulation during the 200 year simulation period.
The DYNco2 levels vary for each of the simulations ranging between 1050 ppmv and 1400 ppmv, but all are still in line with Montenegro et al. [2007] and Eby et al. [2009], as the sources and sinks of CO₂ to and from the atmosphere are modified by changes in the ocean biological pump. The higher concentrations are associated with the positive feedback caused by warming of surface waters and CO₂ outgassing in the reduced albedo experiments and increased respiration in the surface oceans for the reduced settling velocity experiments (Figs. 4.2a and 4.2b). Despite beginning the simulation at 2015 forcing levels, the model cannot utilize the 2015 forcing levels out of the gate, which would be one advantage to a lukewarm start. SSTs warm with a different pattern than the CO₂ forcing alone, thanks to the changes in albedo (Fig. 4.2b). There is a lot of overlap, SSTs rise slowly for Ctrl-280co2, 280co2-Setl, and 400co2 and then level out after about 30 years. 280co2-B and 400co2-B, rise more rapidly in the first 20 years and then level around 30 years. The DYNco2 and Alb simulations both feature continuously rising SSTs to match the rising levels of CO₂. The oxygen concentration falls as SSTs rise for 400co2 and DYNco2, but rises almost continuously for all of the phytoplankton community experiments (Fig. 4.2c).

Figure 4.3 shows anomaly profiles of zonally averaged oxygen concentration with depth, comparing an experimental simulation to the control simulation, Ctrl-280co2 (experimental minus control). Figure 4.3 also shows hypoxia (dissolved O₂ < 60 μmol L⁻¹) for the experiment and control simulations. Generally speaking, the simulations where only atmospheric forcing was changed (Figs. 4.3a and 4.3b) show decreased O₂ concentrations everywhere, with the exception of a small increase in O₂ above the
Antarctic continental shelf. DYNco2 has much larger negative anomalies in oxygen, well below -60 μmol L\(^{-1}\) for large stretches of ocean (Fig. 4.3b). The region of hypoxia is also the largest with DYNco2 for those experiments driven exclusively by changes in CO\(_2\). Negative anomalies are much smaller for 400co2, but there is still a notable increase in hypoxia around 200 m, just below the photic zone (Fig. 4.3a).

The oxygen anomalies for the altered phytoplankton community experiments are more mixed, but generally, entirely negative below the photic zone. Both 280co2-B (Fig. 4.3c) and 400co2-B (Fig. 4.3b) exhibit reductions in oxygen in the subtropical photic zone, with the magnitude being relatively close to each other as well (around -40 μmol L\(^{-1}\)), but below this (and in the tropics below around 100 m), the anomalies are almost entirely positive and of fairly high magnitude (> 60 μmol L\(^{-1}\)). DYNco2-B has much higher magnitude negative anomalies just below the photic zone (Fig. 4.3e), with large portions < -60 μmol L\(^{-1}\). The positive anomaly in the tropics is also smaller latitudinally than 280co2-B or 400co2-B, but the magnitude in the middle of the anomaly is just as large (Fig. 4.3e).

For the experiments where only albedo was changed (280co2-Alb, Fig. 4.3f and DYNco2-Alb, Fig. 4.3g), oxygen concentrations decrease quite strongly, particularly for DYNco2-Alb (Fig. 4.3g) where large stretches of ocean above the thermocline feature anomalies below -60 μmol L\(^{-1}\) in both hemispheres. The largest regions of hypoxia are also present for DYNco2-Alb (Fig. 4.3g). In simulations where only settling velocities were altered (Figs. 4.3h and 4.3i), we see a similar pattern to the whole phytoplankton community changes (Figs. 4.3c and 4.3e), but with a smaller magnitude in negative
oxygen anomalies just below the surface and larger magnitude positive anomalies below
the photic zone.
Figure 4.3: Zonally averaged dissolved oxygen profile (μmol L$^{-1}$) and hypoxia (dissolved O$_2$ < 60 μmol L$^{-1}$) for a) 400co2 – Ctrl-280co2, b) DYNco2 – Ctrl-280co2, c)280co2-B – Ctrl-280co2, d) 400co2-B – Ctrl-280co2, e) DYNco2-B – Ctrl280co2, f) 280co2-Alb – Ctrl-280co2, g) DYNco2-Alb – Ctrl-280co2, h) 280co2-Setl – Ctrl-280co2, and i) DYNco2-Setl – Ctrl-280co2. Negative values (warm colors) represent regions of decreased dissolved O$_2$ for the respective experimental simulation relative to Ctrl-280co2. Black dashed lines represent hypoxia for the respective experimental simulation, while the very small green spot in each panel represents hypoxia for Ctrl-280co2. See Table 4.1 for abbreviations.
4.3.2. 400co2 vs. Ctrl-280co2 and business-as-usual

Figure 4.4 shows the dissolved oxygen anomalies and hypoxia at 1300 m, the anomalies in sea surface temperatures (SSTs, °C), anomalies in detrital export (μmol N L\(^{-1}\) yr\(^{-1}\)) at 1100 m, and the anomalies in meridional overturning circulation (MOC, Sv) for 400co2 – Ctrl-280co2. Overall the dissolved oxygen concentration at 1300 m (chosen as representative of the level just below the thermocline) is similar for the two simulations (Fig. 4.4a), with the Pacific containing mainly negative anomalies (less dissolved O\(_2\) for 400co2) and the Atlantic containing mainly positive anomalies. The largest negative anomalies (–40 μmol L\(^{-1}\)) tend to be in the Southern Ocean surrounding Antarctica, and this generally agrees with the oxygen profile in Fig. 4.3a. The other large difference is related to hypoxia. As shown in Fig. 4.3b, the increased CO\(_2\) radiative forcing has increased SSTs for 400co2 (Fig. 4.4b), with the warmest anomalies (~3.5°C) being south of Greenland. Export of detritus is relatively similar across the globe at 1100 m (Fig. 4.4c), with the exception of the Eastern Tropical Pacific (EPAC) off the coast of South America. A couplet of enhanced and reduced export by the 400co2 simulation is likely related to shifts in tropical upwelling in the area. Figure 4.4d shows the anomalies in MOC, which are somewhat mixed, but there is a slowing of MOC by about 2-2.5 Sv in the Northern Hemisphere below our thermocline.
Figure 4.4: a) 400co2 – Ctrl-280co2 dissolved oxygen anomalies (μmol L⁻¹) and hypoxia (< 60 μmol L⁻¹) at 1300 m depth. Negative values (warm colors) represent regions where 400co2 has a lower dissolved O₂ concentration relative to Ctrl-280co2. The diagonal hatched areas enclosed by the black dashed line represent hypoxia for 400co2 and the vertical hatched areas enclosed by the green dot-dash line represent hypoxia for Ctrl-280co2. b) 400co2 – Ctrl-280co2 anomalies in sea surface temperatures (SSTs, °C). Positive values (warm colors) represent warmer SSTs for 400co2 relative to Ctrl-280co2. c) 400co2 – Ctrl-280co2 anomalies in detrital export (μmol N L⁻¹ yr⁻¹) at 1100 m depth. Positive values (warm colors) indicate regions of enhanced detrital export for 400co2 relative to Ctrl-280co2. d) 400co2 – Ctrl-280co2 meridional overturning circulation (MOC, Sv) anomalies. Negative values (warm colors outlined by dashed lines) represent regions of reduced MOC for 400co2 relative to Ctrl-280co2.

Figure 4.5 shows DYNco2 – Ctrl-280co2 anomalies. Dissolved oxygen anomalies are mainly negative, but relatively small in magnitude (Fig. 4.5a), with the largest anomalies on the eastern coast of South America and east of the Antarctic Peninsula.
Hypoxia has only slightly expanded for DYNco2 relative to Ctrl-280co2. This result is not all that surprising given the relatively minute differences in zonally dissolved O2 in Fig. 4.3d around 1300 m depth. SSTs are warmer for DYNco2 than Ctrl-280co2, particularly in the Bering Sea, by ~6°C, which is considerable warming for a large body of water over only 200 years (Fig. 4.5b). Figure 4.5c shows the anomalies in detrital export, and the result is largely unchanged from the 400co2 – Ctrl-280co2 case (Fig. 4.4c), with the same positive-negative anomaly couplet in the EPAC, likely demonstrating the climatic impact on upwelling in that region. The spatial area and magnitude of that couplet have expanded relative to 400co2. Anomalies in MOC (Fig. 4.5d) are slightly larger than those seen in 400co2 (Fig. 4.4d) but of a similar pattern. In the Southern Hemisphere, there is a clear reduction in MOC around 600 m, less than -5 Sv, but this does not seem to result in reduced oxygen below the thermocline (Fig. 4.5a).
Figure 4.5: As in Fig. 4.4, but for DYNco2 – Ctrl-280co2.

4.3.3. Impact of changes to the phytoplankton community (albedo and settling)

Figure 4.6 shows the anomalies for 280co2-B – Ctrl-280co2. The dissolved oxygen at 1300 m (Fig. 4.6a) is dominated by positive anomalies with values peaking above 80 μmol L⁻¹ on the Central American Pacific coast and in the northern Indian Ocean. Hypoxia is only present for Ctrl-280co2 at 1300 m, but it is important to remember that higher in the water column, 280co2-B does show some negative zonally averaged oxygen anomalies (Fig. 4.3c). Anomalies in SSTs are mainly positive, a direct result of the reduction in surface albedo. The majority of the Western Pacific Ocean is
between 4-6°C warmer in 280co2-B than in Ctrl-280co2 (Fig. 4.6b), showing that the surface albedo has a stronger impact on ocean temperatures than the CO₂ forcing. This might help to explain some of the negative oxygen anomalies near the surface in Fig. 4.3c.

The results shown in Fig. 4.7 enhances this argument. Figure 4.7a shows anomalies in surface air temperature (°C), which are entirely positive despite the same CO₂ forcing (this also shows the very strong impact of the oceans across the entire globe). Figure 4.7b shows the net radiation (W m⁻²) at the top of the atmosphere, and we can see more positive net radiation over the oceans, due to the decreased albedo, and reduced net radiation over the continents. Detrital export anomalies at 1100 m are almost entirely negative (Fig. 4.6c), which makes sense, as slower detrital velocities would favor less detritus exiting the thermocline. As with 400co2 (Fig. 4.4c), the most notable anomalies exist in the EPAC, but other large positive anomalies exist in favored tropical upwelling zones on the eastern sides of Africa and Asia (Fig. 4.6c). Anomalies in MOC are mainly negative in the Southern Hemisphere (Fig. 4.6d) and up to -6 Sv in pockets. This is likely tied to decreasing albedo. Despite the slowing of subsurface circulation, the water column still remains well oxygenated (Fig. 4.3c). A pocket of increased MOC is present in the Northern Hemisphere around the thermocline (Fig. 4.6d).
Figure 4.6: As in Fig. 4.4, but for 280co2-B – Ctrl-280co2.
Figure 4.7: a) Surface air temperature anomalies (°C) for 280co2-B – Ctrl-280co2 where positive values (warmer colors) indicate warmer air temperatures for 280co2-B relative to Ctrl-280co2. b) Net radiation anomalies at the top of the atmosphere (W m$^{-2}$) for 280co2-B – Ctrl-280co2 where positive values (warm colors) indicate increased net radiation for 280co2-B relative to Ctrl-280co2.

Figure 4.8 shows the anomalies for 400co2-B – Ctrl-280co2. In a general sense, the patterns are similar to 280co2-B – Ctrl-280co2 (Fig. 4.6), but of a different magnitude. Dissolved oxygen anomalies at 1300 m are generally entirely positive (Fig. 4.8a), but they are slightly smaller than those for 280co2-B – Ctrl-280co2 (Fig. 4.6a). Anomalies in the SSTs are again entirely positive, with peaks just over 7°C south of Greenland (Fig. 4.8b). This warming likely explains the slightly smaller positive anomalies in dissolved oxygen at 1300 m than 280co2-B (Figs. 4.8a and 4.6a, respectively). The anomalies in detrital export at 1100 m (Fig. 4.8c) and in MOC (Fig. 4.8d) are similar to those shown in Figs. 4.6c and 4.6d. This shows the overall control of the settling velocity on export below the thermocline and the relative control of albedo and stratification of the water column on impacting the MOC.
Figure 4.8: As in Fig. 4.4, but for 400co2-B – Ctrl-280co2.

Figure 4.9 shows the anomalies in the same variables as above for DYNco2-B – Ctrl-280co2. The anomalies in dissolved oxygen at 1300 m are mainly positive in the Northern Hemisphere and tropics, negative in mid and high latitudes in the Southern Hemisphere, but the magnitudes are relatively small. DYNco2-B SSTs are much warmer at year 2200 (Fig. 4.9b), with large regions of anomalies passing 12°C (again, note the change in scales). Detrital export (Fig. 4.9c) shows the same general pattern as the phytoplankton dynamics experiments, with large negative values near tropical upwelling zones on the west coast of the continents. Figure 4.9d shows the MOC anomalies, which
are very similar to those in DYNco2 – Ctrl-280co2, but the magnitudes (in both directions) are magnified.

Figure 4.9: As in Fig. 4.4, but for DYNco2-B – Ctrl-280co2.

4.3.4. Albedo and settling velocities on their own

Figures 4.10 and 4.11 describe results of the two experiments where only albedo was decreased for the 280co2 and DYNco2 levels. Figure 4.10 shows the anomalies for 280co2-Alb – Ctrl-280 co2. Anomalies in dissolved O$_2$ at 1100 m are mainly negative, except for some large patches in the Western Pacific and Western Atlantic Oceans (Fig.
4.10a. Hypoxia for 280co2-Alb matches with Ctrl-280co2 fairly well with some slight expansion in the equatorial EPAC and some contraction near Japan and Korea. SSTs are warmer over the entire globe (Fig. 4.10b), with the Western Pacific containing the strongest warming in the Western Pacific, near 5°C, almost exactly matching 280co2-B – Ctrl-280co2 (Fig. 4.6b). Export of detritus (Fig. 4.10c) contains the same positive-negative anomaly couplet in the EPAC as 400co2 – Ctrl-280co2 (Fig. 4.4c) and DYNco2 – Ctrl-280co2 (Fig. 4.5c), but with magnitude slightly larger (less) than 400co2 – Ctrl-280co2 (DYNco2 – Ctrl-280co2). The anomalies in MOC (Fig. 4.10d) mirror the anomalies in 280co2-B – Ctrl-280co2 (Fig. 4.6d) quite well, almost exactly.

Dissolved oxygen anomalies for DYNco2-Alb – Ctrl-280co2 (Fig. 4.11a) show a remarkably similar pattern to 280co2-Alb – Ctrl-280co2 (Fig. 4.10a). Largely negative anomalies in the Southern Ocean and EPAC, with some positive anomalies in the same ocean basins (Pacific and southwestern Atlantic), which are also generally smaller magnitude. The spread and contraction of hypoxia relative to Ctrl-280co2 is also strikingly similar between the two albedo experiments. SSTs are much warmer for DYNco2-Alb than Ctrl-280co2, with pockets of the Western Pacific eclipsing 12°C (Fig. 4.11b). The positive-negative export anomaly couplet in the EPAC is now at its highest magnitude (Fig. 4.11c) for DYNco2-Alb – Ctrl-280co2. MOC anomalies (Fig. 4.11d) are again nearly identical to those of DYNco2-B (Fig. 4.9d), showing that albedo has the larger impact on MOC changes of those we are considering for this research.
Figure 4.10: As in Fig. 4.4, but for 280co2-Alb – Ctrl-280co2.
Figure 4.11: As in Fig. 4.4, but for DYNco2-Alb – Ctrl-280co2.

Anomalies for reduced settling velocity alone are shown in Figs. 4.12 and 4.13. Figure 4.12 presents the anomalies in dissolved O$_2$ at 1300 m (Fig. 4.12a) and the detrital export anomalies at 1100 m (Fig. 4.12b). A change in the particle settling velocities alone will have no impact on SSTs or on MOC over the course of 200 years, so the values are the same as those for Ctrl-280co2 globally. Dissolved oxygen anomalies are mainly positive, and relatively large (Fig. 4.12a). Regions of hypoxia at 1300 m do not exist (Fig. 4.12a). As with the phytoplankton community experiments, the anomalies in detrital
export are the largest (and most negative) near tropical west coast upwelling zones (Fig. 4.12b, compared to Figs. 4.6c, 4.8c, and 4.9c).

![Image](https://via.placeholder.com/150)

**Figure 4.12:** a) As in Fig. 4.4a and b) as in Fig. 4.4c, but for 280co2-Setl – Ctrl-280co2.

Dissolved oxygen for DYNco2-Setl – Ctrl-280co2 (Fig. 4.13a) shows mainly positive anomalies globally. The majority of the oceans are better oxygenated under reduced settling speed conditions when compared to the climate only experiment (Fig. 4.5a). Additionally, there is a clear contraction of hypoxia relative to Ctrl-280co2 (Fig. 4.13a). Anomalies in SSTs (Fig. 4.13b) are generally similar in pattern and magnitude to those of DYNco2 – Ctrl-280co2 (Fig. 4.5b), again because settling velocities on their own do little to impact temperatures. Export below the thermocline (Fig. 4.13c) exhibits a similar pattern to 280co2-Setl – Ctrl-280co2 (Fig. 4.12b), and the other phytoplankton community experiments. The MOC anomalies (Fig. 4.13d) are nearly the same as those from DYNco2 – Ctrl-280co2 (Fig. 4.5d), reinforcing the idea that changing settling velocities on their own have almost no impact on ocean temperatures or on overturning.
4.3.5. Hypoxia and anoxia

With changes in climate and falling levels of dissolved oxygen, the development and spread of hypoxia and anoxia both become concerns. Figure 4.14 shows the presence of hypoxia for Ctrl-280co2 (Fig. 4.14a), 400co2 (Fig. 4.14b), and DYNco2 (Fig. 4.14c) at 200 m (taken here as a representation of the bottom of the continental shelf) and 1300 m (the level below the thermocline). The patterns for the three climate related simulations are quite similar, particularly below the thermocline. Intermediate hypoxia is generally
present for all three experiments in the Northern Pacific Ocean between northern Asia and North America, stretching to equatorial South America (Fig. 4.14). Differences are much more prevalent at the shallower continental shelf (200 m) where there is a clear expansion of hypoxia into the Central Pacific for the two warmer climates (Figs. 4.14b and 4.14c), compared to the Ctrl-280co2 (Fig. 4.14a).

**Figure 4.14:** Hypoxia (dissolved O₂ concentration < 60 μmol L⁻¹) at 200 m (vertical hatching outlined by green dot-dash line), 1300 m (horizontal hatching outlined by red dot-dot line), and 3200 m (diagonal hatching outlined by black dashed line) for a) Ctrl-280co2, b) 400co2, and c) DYNco2. Note that none of the 3 experiments here developed hypoxia at 3200 m.

The experiments with modified phytoplankton community only show areas of hypoxia on the continental shelf and they are confined to the Pacific coast of Central America and northern South America (Fig. 4.15). The only exception is a small pocket in
the central Pacific near the International Date Line/Equator intersection and a very small region off of the Asian Pacific Islands for DYNco2-B (Fig. 4.15c). No deep ocean (3200 m depth) hypoxia exists for any simulation, despite the general reduction in oxygen for 400co2 (Fig. 4.2c, red dashed line) and DYNco2 (Fig. 4.2c, orange dash-dot-dot line).

**Figure 4.15:** As in Fig. 4.14, but for a) 280co2-B, b) 400co2-B, and c) DYNco2-B. Note that there is no hypoxia at 1300 m (intermediate depth) or 3200 m (deep ocean) for any of these experiments.

Hypoxia for 280co2-Alb (Fig. 4.16a) and DYNco2-Alb (Fig. 4.16b) is slightly expanded relative to their climate only counterparts (Figs. 4.14a and 4.14b, respectively). This is particularly true for the 200 m depth in 280co2-Alb (Fig. 4.16a), where hypoxia spreads all the way to New Guinea, while in Ctrl-280co2, the hypoxia just advances west
of the International Date Line (Fig. 4.14a). Intermediate depth hypoxia only expands slightly for the two albedo experiments (Fig. 4.16).

**Figure 4.16**: As in Fig. 4.14, but for a) 280co2-Alb and b) DYNco2-Alb. Note that there is no hypoxia present at 3200 m for either experiment.

Hypoxia for 280co2-Setl (Fig. 4.17a) and DYNco2-Setl (Fig. 4.17b) contracts at the 200 m depth, with almost none present in 280co2-Setl (Fig. 4.17a). This is compares well with the phytoplankton community experiments with the same CO₂ concentrations (compare Fig. 4.17a to Fig. 4.15a and Fig. 4.17b to Fig. 4.15c). In addition to contraction at continental shelf depth, hypoxia has disappeared at the intermediate depth (1300 m), matching their phytoplankton community counterparts (Figs. 4.15a and 4.15c).
Anoxia was only simulated at continental shelf depths (with one very small exception), and only for 7 of the 10 experiments. Figure 4.18 shows anoxia for the climate only experiments. Anoxia only covers a few limited regions and does not extend very far from the equator. The largest regions of anoxia exist in DYNco2 (Fig. 4.18c). Despite the decreasing oxygen concentrations for both 400co2 and DYNco2 (Fig. 4.2c, red dashed line, orange dash-dot-dot line), anoxia does not extend below the continental shelf.

Figure 4.19 shows anoxia for 280co2-Alb (Fig. 4.19a) and DYNco2-Alb (Fig. 4.19b). The two albedo experiments have relatively expanded anoxia at 200 m depths, but like their climate only counterparts, it does not extend far from the equator. The only occurrence of anoxia below continental shelf and thermocline depths occurs in the Bay of Bengal for DYNco2-Alb (red dot in Fig. 4.19b), so anoxia might not be out of the question in the intermediate oceans if we have significant warming coupled with more turbid and darker water columns. When the settling velocity alone is reduced, anoxia disappears everywhere.
Figure 4.18: Anoxia (dissolved O₂ concentration < 10 μmol L⁻¹) at 200 m (vertical hatching outlined by green dot-dash line), 1300 m (horizontal hatching outlined by red dot-dot line), and 3200 m (diagonal hatching outlined by black dashed line) for a) Ctrl-280co2, b) 400co2, and c) DYNco2. Note that none of the 3 experiments here developed hypoxia at 1300m or 3200 m.

Figure 4.19: As in Fig. 4.18, but for a) 280co2-Alb and b) DYNco2-Alb. Again, no anoxia is present at 3200 m for any of the experiments.
4.4. Discussion

4.4.1. Impacts of climate change

Climate plays an important role on the formation and spread of hypoxia-anoxia, but in many simulations of deep past climate states, climate and its impacts on ocean dynamics are not sufficient to promote the spread of hypoxia-anoxia [Misumi and Yamanaka, 2008; Montenegro et al., 2011; Ozaki et al., 2011; Monteiro et al., 2012; D’Amico et al., 2017], and some other factor, such as a change in nutrient concentrations or biogeochemical cycling was necessary for modeling of widespread ocean anoxia. In the modern world, climate and environmental change are occurring very rapidly and the impacts on our land, oceans, and ecosystems are already showing signs of consequences. One of those consequences is the expansion of oxygen minimum zones which contribute to dead zones [Stramma et al., 2008, Deutsch et al., 2011] where macroorganisms cannot survive.

In the 400co2 and DYNco2 experiments, we note a general decrease in dissolved oxygen compared to Ctrl-280co2 in both global (Fig. 4.2c, compare red dashed, orange dash-dash-dot, and black solid lines) and zonal averages (Figs. 4.3a and 4.3d). The slight reduction in ocean oxygen near the surface can be attributed to decreased dissolution of atmospheric oxygen into the oceans with warmer surface temperatures [García and Gordon, 1992]. SSTs for both 400co2 (Fig. 4.4b) and DYNco2 (Fig. 4.5b) were higher globally leading to reduced oxygen at the surface. Warming climates also tend to have impacts on MOC, which serves as the ventilation system of the deep oceans, keeping them well oxygenated [Matear and Hurst, 2003; Butterfield, 2009]. Warmer oceans
might lead to a more sluggish circulation and reduced delivery of oxygen to depths, but we do not note a major reduction in MOC in the 400co2 experiment (Fig. 4.4d). The DYNco2 experiment (Fig. 4.5d) has larger reductions in MOC, but this still does not translate to spread of hypoxia or large reductions in intermediate or deep ocean oxygen. The reductions in subsurface oxygen are much subtler for both 400co2 and DYNco2, as the deep oceans and surface oceans are maintaining communication. As detritus falls through the water column, it is remineralized, consuming oxygen. Export for 400co2 (Fig. 4.4c) and DYNco2 (Fig. 4.5c) at 1100 m did not vary all that much from Ctrl-280co2, outside of the tropical upwelling zone in the EPAC, where a clear couplet existed, likely due to climate induced shifts in the upwelling zone.

These simulations of climate change show hypoxia at 200 m, on the continental shelf, and at 1300 m, below the thermocline. Additionally, the preindustrial simulation (Ctrl-280co2) contained similar levels of hypoxia to the 400co2 and the DYNco2 (Figs. 4.14a, 4.14b, and 4.14c) after 200 years of simulation. Locations of hypoxia are normally not well simulated, particularly in a global model like the UVic ESCM. Subgrid scale hypoxic-anoxic dead zones might exist in several locations, as discussed in Schmittner et al. [2008], but these must be studied with higher resolution regional models [Meier et al., 2011] or seasonal localized models [Tyson and Pearson, 1991]. On a purely qualitative basis, our results from the pure climate simulations agree with Bopp et al. [2002], Matear and Hirst [2003], Schmittner et al. [2008], and Yamamoto et al. [2014], but a longer analysis with a more rigorous estimated carbon dataset could help our model compare with these works quantitatively. Some disagreement between the modeling efforts can
certainly be related to differences in timing and model setup as well. While oxygen concentrations in the oceans are certainly impacted by climate, spread of hypoxia-anoxia is not favored in UVic ESCM by climate change alone.

4.4.2. Detrital settling velocities and ocean surface albedo

Biological and biogeochemical changes have also been viewed as necessary for spread and proliferation of hypoxic-anoxic ocean waters [Misumi and Yamanaka, 2008; Butterfield, 2009; Montenegro et al., 2011; Ozaki et al., 2011; Monteiro et al., 2012; Melchin et al., 2013; D’Amico et al., under revision]. Although we do not test the impact of nutrients or eutrophication in this study [Diaz, 2001; D’Amico et al., under revision], we do test changes to the biological pump hypothesized by Butterfield [2009] and Mouw et al. [2016]. We slowed down the settling velocities of detritus and decreased the ocean surface albedo to mimic the cyanobacterially dominated, turbid, stratified water column that would contribute to deoxygenation.

The change in phytoplankton community (both reduced albedo and settling velocities) did not contribute to reductions in mid-ocean or deep ocean oxygen (Figs. 4.3b, 4.3c, and 4.3d) but there is some diminishing of oxygen near the ocean surface for each of these. The largest depletion of surface oxygen occurs for the warmest climate scenario (DYNco2-B, Fig. 4.3d). This warming can probably be linked to albedo, as we saw in the albedo only experiments, which again will contribute to decreased dissolution of oxygen in the water column. Albedo did play a role in stratification for the phytoplankton community experiments, and large portions of the Northern Hemisphere deep ocean saw a reduction in MOC (Figs. 4.6d and 4.8d), but this clearly had little
impact on the oxygen at depth (Figs. 4.6a and 4.8a). Albedo generally did slow overturning, particularly in the Northern Hemisphere for DYNco2-Alb (Fig. 4.11d); this may have contributed to expansion of hypoxia in the intermediate depths, but not the deep oceans. The largest regions of hypoxia were generally present in the albedo only experiments.

Clearly the sinking of detritus has had impacts on the export of detritus below the thermocline (Figs. 4.7c, 4.9c, 4.10c, 4.12b, and 4.13c), particularly in the upwelling zones on the eastern coasts of tropical continents, but this was expected. Slower particle fall speeds contribute to more remineralization and fast recycling near the surface, meaning less detritus near and below the thermocline. Less detritus below the thermocline leads to reduced oxidation and remineralization of falling particles and no additional uptake of O$_2$ in the intermediate and deep oceans, meaning higher O$_2$ concentrations. The variable plankton communities hypothesis has some promise, but from our testing, it appears that the hypothesis works best when in shallower water columns, perhaps associated with a shallow continental shelf section. The impact of settling velocities appears limited when dealing with intermediate or deep ocean hypoxia-anoxia in the UVic ESCM.

A larger conclusion also emerges from the biological pump experiments. In a world of rising atmospheric CO$_2$ concentrations and SSTs, if the makeup of the phytoplankton community does indeed shift to slower-sinking and smaller cyanobacteria over large stretches of the oceans, this would tend to counteract the impacts of decreasing dissolved oxygen due to rising temperatures, particularly in the intermediate oceans and
deep oceans. DYNco2-B had extremely large temperature changes relative to Ctrl-280co2 (Fig. 4.10b) but the intermediate depth tropical Pacific showed increased dissolved O\textsubscript{2} concentrations at year 2200 (Fig. 4.10a) and no intermediate hypoxia existed. When settling velocity was changed independent of albedo, results were similar, but somewhat amplified. With reduced particle fall velocities we see a modest increase in deep and intermediate ocean oxygen and an elimination of intermediate depth hypoxia.

If following the example of the UVic ESCM here and of Mouw et al. [2016] and Mousing et al. [2017], where warming leads to a shift to smaller and more cyanobacterially-dominated phytoplankton, we might need to reconsider some of our hypotheses regarding reduced ocean oxygen in a warming world. Slower particle velocities potentially have the ability to offset warming induced reductions in dissolved oxygen in the intermediate and deep oceans, as remineralization and respiration occur above the thermocline. In this case, remineralized particles are never delivered below the thermocline and the waters remain well ventilated. Oxygen in the surface layer can still be somewhat reduced due to decreased dissolution of atmospheric O\textsubscript{2}, but they still remain in contact with the atmosphere, so one could argue that oxygenation increases as a whole when particle velocities are slowed.

4.5. Chapter 4 Conclusions

The UVic ESCM is used here to test a series of factors that might impact deep and mid ocean oxygenation in the near and more distant future. We test three levels of CO\textsubscript{2}, 280 ppmv (preindustrial), 400 ppmv (2016/2017) and an IPCC A2 type business as usual simulation beginning with 2015 concentrations of CO\textsubscript{2}, which results in concentrations of
1050-1400 ppmv at the end of year 2200. We also tested variations to the phytoplankton community and its potential impact on the development of oceanic hypoxia-anoxia in the presence of an oxygen rich atmosphere, namely slowing the detrital settling velocity and reducing the ocean surface albedo to create a more turbid and stratified water column.

Warming the climate by increasing CO₂ forcing does contribute to a general reduction in oxygen concentration in the oceans, as oxygen is less soluble in warmer waters. Although limited reductions in overturning were noted, these seemed to not have a large impact on the oxygenation of the intermediate and deep oceans; it appears the surface ocean and deep oceans maintain communication when only the temperatures increase, which keeps the deep oceans well ventilated. Small reductions in deep ocean oxygen are noted, as less oxygen is available to the deep oceans due to solubility at the surface, but this has little impact on the spread of hypoxia-anoxia.

When reducing albedo and settling velocities, there is a slight decrease in oxygen just below the ocean surface, but the intermediate and deep oceans actually become more oxygenated. As the particles fall more slowly in the surface ocean, remineralization and fast recycling are more efficient, so fewer particles will actually fall below the thermocline and be oxidized in the intermediate and deep oceans. The biological pump hypothesis does show some promise in shallower and potentially disconnected basins (epeiric), as the reduction in albedo does contribute to increased stratification and less oxygen just below the surface, but again, its impacts were not felt in the intermediate or deep oceans, as no hypoxia is simulated when reducing both albedo and detrital settling velocities in the UVic ESCM. Additionally, because of the biological pump experiments
here, we might need to question the true role of warming in deep and intermediate ocean oxygen concentrations. Warming will decrease solubility, but if the phytoplankton community were to shift to a more cyanobacterially, slow-sinking stage in response to warming, then according to the UVic ESCM, dissolved oxygen concentrations would actually increase, particularly in the intermediate depths. To our knowledge, we are the first modeling group to come to this conclusion, so additional studies with multiple models and sensitivity analyses are certainly required.

In order to improve our simulations and align them better with changes we are experiencing today, we would like to design a more contemporary CO$_2$ dataset to use with the business-as-usual simulations, so that we can extend the experiments well beyond 200 years. A longer time period and more simulation will also help to strengthen this new hypothesis; if warming oceans do indeed shift to more slow-sinking and smaller particles, then this could help to offset some of the climate warming related deoxygenation we expect to occur in the near future.
Chapter 5. Dissertation Conclusions

This dissertation utilizes the UVic ESCM to test several hypotheses that are linked to depletion of deep or intermediate ocean dissolved oxygen. In various capacities, the impacts of climate change, atmospheric oxygen, atmospheric dynamics, ocean dynamics, nutrients, and changes to the biological pump are tested. While no definitive answers for spread of anoxia in the Late Ordovician or the future of oxygen in our oceans are presented, this research has provided additional clarity of the problem (albeit with only one ESCM).

The main contributors to anoxia in the deep ocean and on the continental shelf with Late Ordovician paleogeography are low concentrations of atmospheric oxygen, enhancement of NO$_3$, and reduction in ocean albedo. Qualitatively, the oxygen in the atmosphere has the strongest impact on the oxygen concentrations in the oceans, which makes sense, as the atmosphere is by far the largest source of oxygen to the ocean and oxygen saturation is directly linked to the amount present in the atmosphere (photosynthesis in the photic zone provides a very small percentage of the total ocean dissolved oxygen). Every experiment that featured low oxygen had expanded anoxia relative to the higher oxygen experiment. The concentration of NO$_3$ also had a very large impact, particularly away from the tropical hot spots for anoxia in the Northern Hemisphere. Reducing albedo also led to a slight expansion of anoxia, but did feature
heavy depletion of deep ocean oxygen in the Southern Hemisphere, in the vicinity of the largest landmass.

Warming the climate played a very minor role in the expansion of anoxia during the Late Ordovician; warmer climates were certainly more favorable for the development of anoxia, but played very little role in its expansion, particularly in the deep oceans. Addition of PO$_4$ did enhance NPP in the Tropics, but never had the large impact on deep ocean or continental shelf anoxia produced by NO$_3$. The experiments with increased remineralization rates and reduced detrital settling velocities do show some limited promise. Enhancing remineralization increases the amount of PO$_4$ available in the surface ocean, but the enhancement to NPP is minimal outside of the Tropics and resulted in increased oxygenation in the deep oceans. When increasing the remineralization rates, the focus is within the surface oceans, so fewer particles reach the deep oceans and oxygen can continue to accumulate with deep ocean ventilation. Slowing the settling velocities also reduces the export of material from above the thermocline to the deep oceans. These two potential causes for oxygen reduction are more favorable in shallow water columns, where deep water does not exist.

The present day and future oceans are not likely to experience lower atmospheric oxygen concentrations, and inputs of NO$_3$ will be limited to highly productive river basins, so the spread of anoxia in the intermediate and deep oceans is unlikely. However, climate and environmental changes are occurring at rapid pace (e.g., rapidly increasing levels of atmospheric CO$_2$, increased ocean acidification, depletion of Arctic sea ice), which may have a role in the reduction of oxygen concentrations in the future oceans.
Warming from enhanced levels of atmospheric CO₂ (relative to preindustrial) do contribute to a decrease in dissolved oxygen at intermediate depths, from a reduction in the dissolution of oxygen in warmer ocean waters. Although overturning slowed slightly, it was insufficient to reduce the ventilation of the intermediate and deep oceans in 200 years. Mid-ocean hypoxia was present in all climate related experiments (including preindustrial) and the hypoxic region did not expand with warmer climates. Despite decreasing oxygen concentrations in the two climate warming experiments, the hypoxic regions actually shrunk with time. Reduction of detrital settling velocities and surface albedo (simultaneously) exhibit a modest reduction in dissolved oxygen just below the ocean surface, but also increase oxygen concentrations in the intermediate ocean while eliminating hypoxia at that depth. Decreasing albedo alone will generally work to deplete oxygen, but this change cannot happen without increased turbidity due to either slower particle sinking or enhanced nutrient loadings. Slow detrital fall speeds alone will tend to either maintain or enhance oxygen concentrations in the deep and intermediate oceans. Because of these experiments, it is likely that a reexamination of the role of particle sinking in a warming ocean is warranted in future work. If a warming ocean does indeed contribute to domination by small, slow-sinking cyanobacteria, then this might counteract the decreased dissolution of oxygen and increase dissolved oxygen for vast portions of the ocean.

The results from this dissertation research has opened several new avenues into modeling deep and intermediate ocean oxygen. Although this dissertation has not examined every possible factor potentially depleting ocean oxygen, new avenues
regarding albedo, settling velocities, and remineralization were explored. Improvements can be made in various experiments throughout this dissertation, which include, but are not limited to, improving the Ordovician winds with an atmosphere general circulation model, determining if glacial ice is present on Gondwana, varying Ordovician sea levels to test how the Gondwanan glaciation may have impacted oxygen, testing alternative paleogeographic reconstructions for the Ordovician and Silurian, separating the shallow and deep oceans for improved remineralization, and creating a more up-to-date CO$_2$ forcing dataset for the future experiments. Nonetheless, this dissertation has explored many mechanisms affecting oceanic oxygen, and identified new experiments that are possible with climate, ocean, biogeochemical, or coupled models.
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Appendix A: Model validation of the UVic ESCM with an Ordovician solar constant

Here we compare the UVic ESCM simulated Ordovician climate to previous modeling and observational studies for the time period. This comparison is challenging as the models discussed all feature different experimental setups and boundary conditions, so a true one-to-one relationship between model results should not be expected. Figure A.1 compares the air temperatures at sea level for the control experiment with solar constant of 1313 W m$^{-2}$, a 4% reduction in relation to its present value of 1368 W m$^{-2}$ (Ctrl-RSC, Fig. A.1a) and the climate modeling study of Herrmann et al. [2004a] with Late Katian (Ashgillian, ~458-443 Ma) paleogeography and high sea level (Fig. A.1b). Both of the latter simulations feature 12xPAL levels of atmospheric CO$_2$ and a reduction of the solar constant by around 4%. Figure A.2 compares the air temperatures simulated Ctrl-RSC with those from the weathering model simulations of Porada et al. [2016]. The simulations of Porada et al. [2016] feature 8xPAL CO$_2$ with a solar input value of 1319 W m$^{-2}$ and a cold summer orbital configuration.

It is fairly clear that the Ctrl-RSC has generally warmer surface temperatures (Fig. A.1a), as temperatures top out above 30°C across the entire equator, while Herrmann et al. [2004a] only have a few pockets above 30°C over Gondwana and Baltica. However, the current study shows a similar pattern, with the hottest temperatures over these same regions and generally of similar magnitude. Figures A.1a and A.1b exhibit similar
patterns and agree fairly well around the poles, where the temperatures indicated by our current study are more on par with those of Herrmann et al. [2004a].

**Figure A.1**: Air temperature (°C) at sea level for a) the control (Ctrl-RSC) UVic ESCM simulation and b) the atmospheric modeling simulation of Herrmann et al. [2004a].

The results from Ctrl-RSC (Fig. A.2a) compare reasonably well to Porada et al. [2016] (Fig. A.2b), despite vastly different paleogeography and sea level between the two studies. Porada et al. [2016] only highlighted the air temperature above the land surface, which as discussed above, also contains topography. The two simulations are remarkably similar in the tropics, even with clear differences in the two model resolutions. The Ctrl-RSC has a somewhat narrower swath of temperatures above 35°C and no pockets between 45-55°C. Temperatures over Laurentia and Baltica are quite similar despite difference in paleocontinent shape. Over Gondwana, the Ctrl-RSC temperatures are somewhat higher, with no area below 5°C, but this can be attributed to the larger land area and reduced sea level featured in Porada et al. [2016]. This research cannot address
these issues, as the UVic ESCM needs to have wind data for a given dataset of paleogeography in order to run properly.

Figure A.2: As in Fig. A.1, but with b) the mean annual air temperature from the chemical weathering modeling of Porada et al. [2016].

Like the surface air temperature, the sea surface temperatures (SSTs, Figs. A.3 and A.4) follow a similar pattern to the air temperatures at sea level. Figure A.3b features the SSTs for Herrmann et al. [2004b], with Late Katian (Ashgill) paleogeography, high sea level, and 15xPAL atmospheric CO$_2$ levels, while Fig. A.3a features SSTs for the Ctrl-RSC experiment. The Ctrl-RSC experiment features higher SSTs, particularly in the tropics. The pattern among Figs. A.3a and A.3b is quite similar again, with the warmest waters in the tropics, and temperatures decreasing poleward, although the area with warmest waters in the Ctrl-RSC simulation is found to the north of the warmest waters in Herrmann et al. [2004a] results which are more focused in the southern hemisphere. Both of the climate models feature similar SSTs around the poles, with neither having any surface seawater below 0°C and only a very small area between +2°C and 0°C. Despite
the higher temperatures in the Ctrl-RSC simulation, the equator-to-pole SSTs gradient is similar to the gradient from Herrmann et al. [2004b].

Figure A.3: Sea surface temperatures (SSTs, °C) for a) the control (Ctrl-RSC) UVic ESCM simulation and b) the ocean general circulation model study of Herrmann et al. [2004b].

Figure A.4: As in Fig. A.3, but with b) the sea surface temperatures (SSTs, °C) from the ocean-atmosphere general circulation model study of Pohl et al. [2014].

It should be noted that Herrmann et al. [2004a; b] utilized GENESIS version 2.0 [Thompson and Pollard, 1997], which includes a more comprehensive representation of
atmospheric physics and dynamics, with parameterizations for clouds and convection. Cloud feedbacks could have an additional cooling effect that is not captured by the UVic ESCM EMBM atmosphere quite as effectively by the cloud feedbacks in the specified atmospheric albedo. Cloudiness and convection should both limit surface temperatures to a larger degree than simple changes in albedo and impact the overall temperature distribution through releases of latent heat in the atmosphere. Additionally, the modeling studies of Herrmann et al. [2004 a; b] feature 2°x2° resolution compared to 3.6°x1.8° for the UVic ESCM simulations. While these small differences in resolution would likely have negligible impact on the simulations, it may be that some processes, such as cloud response, are highly scale dependent [Collins et al., 2004]. This could be a potential area for future study with the UVic ESCM.

Figure A.4 compares the Ctrl-RSC (Fig. A.4a) and the SSTs modeled using the ocean-atmosphere GCM of Pohl et al. [2014] (Fig. A.4b). Both simulations feature 12xPAL CO₂ for time periods that can be described as Katian. A few notable differences exist, despite relatively similar patterns. The tropical areas of Pohl et al. [2014] feature only very small regions where SSTs approach 35°C and there is a clear upwelling of cooler waters near the equator (Fig. A.4b). The Ctrl-RSC has a wide swath of SSTs which are likely above 35°C and upwelling is masked by waters that are still warm. Another difference is in the northern hemisphere high latitudes, where SSTs from Ctrl-RSC are much cooler (Fig. A.4a) than those in Pohl et al. [2014], where temperatures are only slightly below 5°C (Fig. A.4b).
The major differences can be attributed to the differences in the two models, the UVic ESCM and the Fast Ocean Atmosphere Model [Jacob, 1997], but can also be attributed to configurations of the simulations. Clearly, there is a difference in the paleogeography and sea level, but the biggest impacts of this exist in the southern hemisphere. Pohl et al. [2014] also utilize a “cold summer orbit”, which should favor cooling in the southern hemisphere (the cool is relative to the majority of landmasses) and a relatively warmer northern hemisphere. This helps to explain the significant cooling in the Ctrl-RSC northern hemisphere SSTs relative to Pohl et al. [2014]. The representation of tropical upwelling in the Ctrl-RSC seems to be slightly washed out relative to Pohl et al. [2014], potentially due to our attempts to match color tables. The remainder of the tropical warmth probably stems from the different model responses to CO₂, solar, and orbital forcing in conjunction with differences in grid resolution of the two simulations.

Vandenbroucke et al. [2009] attempted to validate Late Ordovician climate models with the paleobiogeography of graptolites. The authors concluded that the climate of the middle to earliest Late Ordovician was similar to that of the present day based on assemblages of graptolites, despite much higher concentrations of CO₂. The Ctrl-RSC simulation of the UVic ESCM is in modest agreement with these findings, but tends to be slightly warmer. Warmer waters are more favorable for anoxia however, as the solubility of atmospheric oxygen in the water decreases with warmer conditions. Despite the expected model to model disagreement, the climate simulated by the UVic ESCM reasonably agrees with the Late Ordovician climates simulated by Crowley and Baum.
[1995], Poussart et al. [1999], Herrmann et al. [2004a, b], Pohl et al. [2014], and Porada et al. [2016]. Additionally, the slightly warmer conditions simulated by the UVic ESCM could be more favorable for simulating ocean bottom anoxia, particularly the experiments with the present day solar constant.