Model analysis of ocean carbon storage and transport across climate states

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Abstract
The ocean carbon cycle plays a fundamental role in the Earth's climate system, on decadal to multi-millennial timescales. Of the carbon held in the ocean, the atmosphere, and the terrestrial biosphere combined, more than 90% resides in the ocean. Carbon enters the surface ocean through air-sea gas exchange and from terrestrial sources. It is transported to the deep ocean with the ocean circulation and through the so-called biological pump, where carbon is taken up in the surface ocean by photosynthetic organisms that fall down and decompose at depth. This thesis contributes to the understanding of the processes involved in ocean carbon storage and transport. It examines how these processes respond to model perturbations, and how this response influences our attempts to simulate glacial-interglacial fluctuations in atmospheric carbon dioxide (CO$_2$).

The thesis investigates the response of the simulated ocean carbon storage, and distribution of the isotopic tracer δ$^{13}$C, to changes in physical and biological parameters. In the included studies, we use observational as well as proxy records of oceanic properties to evaluate our model simulations. In addition, we use a climate model to interpret proxy evidence of glacial-interglacial changes in ocean δ$^{13}$C. By using a separation framework, we identify the origin of the carbon in the model ocean, and attribute observed changes to the processes involved.

The results indicate a strong link between ocean carbon storage and the strength of the global ocean overturning circulation. Stronger circulation leads to less carbon storage through a weakening of the biological pump, and through reduced solubility due to an increase in global ocean average temperature.

In simulations of glacial climate, we find that biological adaptability to the surrounding nutrient conditions, through a flexible carbon-to-phosphorus ratio (C/P) in ocean photosynthesis, increases the ocean carbon storage compared to simulations where fixed C/P is applied. The biological flexibility improves the model's ability to reproduce glacial atmospheric CO$_2$. In line with previous research, we find freshwater input to the North Atlantic to be an important factor for reproducing glacial proxy records. The ensemble of simulations that achieve a good representation of glacial-interglacial δ$^{13}$C indicates a deglacial whole-ocean change in δ$^{13}$C of 0.28 ± 0.06‰.

The thesis underlines the importance of the initial state, and the choice of model parameterisations, for the outcome of model ensemble, and intercomparison studies. Finally, it proposes a new method for estimation of ocean carbon transport, and attribution of this transport to different water masses and carbon system processes.

Keywords: Oceanography, Climate, Climate model, Carbon cycle, Paleoclimate.
MODEL ANALYSIS OF OCEAN CARBON STORAGE AND TRANSPORT ACROSS CLIMATE STATES

Malin Ödalen
Model analysis of ocean carbon storage and transport across climate states

Malin Ödalen
This thesis is dedicated to my father Leif, thank you for teaching me to believe in myself
The distant blue, that's me and you
It was from there that we all grew
-Architects
Sammanfattning

Transport och lagring av kol i havet spelar en avgörande roll för klimatsystemet, på kort sikt (årtionden) såväl som på tidsskalor som spänner över tiotusentals år (t.ex. istidscykler). Av den mängd kol som sammanlagt finns lagrad i havet, i atmosfären och i biosfären på land, återfinns 90% i havet. 30% av de mänskliga utsläppen av koldioxid (CO₂) beräknas ha tagits upp av havet, som anses ha haft en avgörande roll för de fluktuationer i atmosfärens koldioxidhalt (hädanefter benämnd pCO₂ atm) som observerats över istidscykler.

Genom gasutbyte med atmosfären, och tillförsel från land, tillförs kol i olika former till havets ytskikt. Detta transporteras sedan vidare till djuphavet, antingen genom oceanicirkulationen, eller genom den så kallade "biologiska pumpen". Den biologiska pumpen innebär att kol tas upp av fotosyntetiserande organismer i ytskiktet, som når de dör faller ned i djuphavet där de bryts ned. Vid nedbrytningen återförs kol till vattnet och har därmed "pumpats" från ytan ned till djuphavet i stort sett oberoende av oceanicirkulationen. När kolet når djuphavet tar det många hundratals år innan det åter kommer i kontakt med atmosfären. Denna avhandling bidrar till att öka kunskapen om de fysiska, kemiska och biologiska processer som bidrar till lagring och transport av kol i havet.

I avhandlingen studeras dessa processer genom klimatmodellsimuleringar. Vi undersöker hur processerna svarar på förändringar av parametrar och drivning i modellen, och vilken roll de har i försök att simulera pCO₂ atm i istidsklimat. Vi studerar hur förändringar i fysiska och biologiska parametrar i vår modell påverkar lagringen av kol, samt förändlingen av isotopen 13C (uttryckt som δ13C), i det simulerade havet. Fördelningen av δ13C i havet är av intresse, då den ger information om cirkulationsmönster och lagring av kol.

För att validera resultaten av våra simuleringar används delvis av nutida observationer från världshaven, och delvis av så kallade proxy–observationer, där bevarade klimatindikatorer tolkas och ger information om forntida klimat. Omvänt använder vi också modellen för att tolka de förändringar i δ13C som antyds av den sparsamma mängd proxy–observationer som finns tillgängliga från den senaste istidscykeln. Vi använder även en metod för att identifiera och separera individuella processers bidrag till mängden kol i havet.

Resultaten indikerar en tydlig koppling mellan mängden kol som lagras i havet och nettostryrkan på oceanicirkulationen, där svagare cirkulation innebär att lagringen av kol ökar. Detta orsakas dels av att den biologiska pumpen förstärks, och dels av att havets medeltemperatur minskar, vilket innebär ökad lösning för CO₂.

I istidsklimat förväntar vi oss en ökad lagring av kol i havet jämfört med sentida, varmare klimat. Simuleringar som väl reproducerar δ13C i enlighet med proxy–observationer från den senaste istidscykeln visar också en ökad lagring av kol, samt en svagare
oceancirkulation, i istidsklimat. Genom att ta hänsyn till fotosyntetiska organismers förmåga att anpassa sig till rådande näringsstillgång i simuleringar av istidsklimat, kan vi förbättra modellens förmåga att reproducerera observerade förändringar i \( pCO_{\text{atm}} \). Vi uppnår 25% ökad lagring av kol i havet jämfört med istidssimuleringar där organismerna inte är anpassningsbara.

I likhet med tidigare studier finner vi att förändringar i färskvattentillförseln till Nordatlanten är en viktig faktor för att modellen ska kunna reproducerade indikerade \( \delta^{13}C \)-mönstren. Tidigare studier har identifierat förändringar i lagring av kol i landväxter som en källa till förändringen i \( \delta^{13}C \) i havet under istidscyklen, då landväxter har en karaktärstypisk reducerad \( \delta^{13}C \)-signatur. En grupp av simuleringar där modellens \( \delta^{13}C \) visar god överensstämmelse med proxy-observationer visar på en medelförändring i \( \delta^{13}C \) på 0.22 – 0.34‰ under den senaste istidscykeln. Detta motsvarar 340 – 520 Pg C (1 Pg C = \( 10^{15} \) g C) från landväxter, som under istiden istället lagrades i vattenmassan.

Denna avhandling tydliggör betydelsen av initialtillståndet och valet av hur en process representeras (parametriseras), för resultatet av jämförelser mellan modellsimuleringar, såväl inom som mellan olika modeller. Dessa slutsatser kan vara av betydelse för planering av framtida jämförelsestudier. Slutligen presenterar avhandlingen en ny metod för att uppskatta omfattningen av koltransport i havet. Denna metod gör det möjligt att tillskriva olika delar av koltransporten till den vattenmassa och den process som den härrör ifrån.
List of Papers

The following papers, referred to in the text by their Roman numerals, are included in this thesis.

PAPER I: **The influence of the ocean circulation state on ocean carbon storage and CO₂ drawdown potential in an Earth system model**

PAPER II: **Variable C/P composition of organic production and its effect on ocean carbon storage in glacial model simulations**

PAPER III: **Earth system model–based analysis of glacial–interglacial changes in ocean δ¹³C**
Ödalen, M., Peterson, C. D., Ridgwell, A., Oliver, K. I. C., Valdes, P. J. *manuscript.*

PAPER IV: **Meridional ocean carbon transport**
Aldama-Campino, A., Fransner, F., Ödalen, M., Groeskamp, S., Yool, A., Döös, K., Nycander, J. *in review for Global Biogeochemical Cycles*

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Papers not included in the thesis:

- **The origin of the negative $\delta^{13}C$ excursion in the Eastern Equatorial Pacific thermocline during the early deglaciation**
  Shao, J., Lowell, S., Menviel, L., Ridgwell, A., Ödalen, M.
  *submitted to PNAS*

- **Seasonal oxygen depletion of a shallow sill fjord on the Swedish west coast**
  doi: 10.1016/j.jmarsys.2017.06.004

- **Consequences of artificial deepwater ventilation in the Bornholm Basin for oxygen conditions, cod reproduction and benthic biomass – a model study**

- **A new phosphorus paradigm for the Baltic Proper**
  Stigebrandt, A., Rahm, L., Viktorsson, L., Ödalen, M., Hall, P.O.J., Liljebladh, B. *Ambio*
Author’s contribution

For **Paper I**, the development of the scientific ideas, as well as the design for the model experiments, was done by me, J. Nycander and K. Oliver in collaboration. I adapted the model code for the experimental design, performed the model simulations, analysed the data and produced the figures. I also did the majority of the writing, and performed the required revisions, with contributions from all co-authors.

For **Paper II**, I had the initial idea of implementing variable C/P composition in cGENIE to examine its role in drawdown of atmospheric CO$_2$. The scientific ideas and experimental setup were then discussed and further developed together with the co–authors. The development of the code was done by me and K. Oliver. I performed all simulations and data analysis, wrote the manuscript and made revisions suggested by the co–authors and reviewers.

Initial analysis for **Paper III** was done by C. Peterson and me, using the ensemble simulations from Paper I. Based on the initial analysis, A. Ridgwell configured and ran the simulations for Paper III. I did the main work on the model–data comparison, with help from C. Peterson. As first author, I have written the manuscript, with small contributions from co–authors, as well as produced all figures.

For **Paper IV**, the initial ideas were put forward by K. Döös, A. Aldama–Campino, and S. Groeskamp. Most of the scientific discussions for the writing of the paper involved A. Aldama–Campino, F. Fransner, S. Groeskamp, and me, with limited contributions by the other co–authors. I have contributed with the detailed knowledge of the global ocean carbon system, carbon partitioning and processes contributing to transport and storage of carbon in the global ocean. I wrote section 2.1, and the text in the Supporting Information. I contributed to the interpretation of results and to the overall writing of the manuscript.
## Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
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<tbody>
<tr>
<td>AABW</td>
<td>Antarctic Bottomwater</td>
</tr>
<tr>
<td>AD</td>
<td>Atmospheric heat diffusivity</td>
</tr>
<tr>
<td>AMOC</td>
<td>Atlantic meridional overturning circulation</td>
</tr>
<tr>
<td>C\text{\textit{carb}}</td>
<td>Hard tissue carbon</td>
</tr>
<tr>
<td>C\text{\textit{dis}}</td>
<td>Disequilibrium carbon</td>
</tr>
<tr>
<td>C\text{\textit{pre}}</td>
<td>Preformed carbon</td>
</tr>
<tr>
<td>C\text{\textit{reg}}</td>
<td>Regenerated carbon</td>
</tr>
<tr>
<td>C\text{\textit{sat}}</td>
<td>Saturation carbon</td>
</tr>
<tr>
<td>C\text{\textit{soft}}</td>
<td>Soft tissue carbon</td>
</tr>
<tr>
<td>C\text{\textit{tot}}</td>
<td>Total carbon</td>
</tr>
<tr>
<td>DD</td>
<td>Diapycnal (vertical) diffusivity</td>
</tr>
<tr>
<td>DIC</td>
<td>Dissolved inorganic carbon</td>
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<tr>
<td>EMIC</td>
<td>Earth system model of intermediate complexity</td>
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<tr>
<td>GAM</td>
<td>Galbraith and Martiny</td>
</tr>
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<td>GCM</td>
<td>General circulation model</td>
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<td>GNADW</td>
<td>Glacial North Atlantic Deepwater</td>
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<tr>
<td>HOL</td>
<td>Holocene</td>
</tr>
<tr>
<td>ID</td>
<td>Isopycnal (horizontal) diffusivity</td>
</tr>
<tr>
<td>LGM</td>
<td>Last Glacial Maximum</td>
</tr>
<tr>
<td>NADW</td>
<td>North Atlantic Deepwater</td>
</tr>
<tr>
<td>OVT</td>
<td>The net strength of the global overturning circulation</td>
</tr>
<tr>
<td>PIES</td>
<td>Pre-industrial equilibrium state</td>
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<tr>
<td>RED</td>
<td>Redfield</td>
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<tr>
<td>SE</td>
<td>Sensitivity experiment</td>
</tr>
<tr>
<td>Sv</td>
<td>Sverdrups</td>
</tr>
<tr>
<td>TC</td>
<td>Total (ocean) carbon storage</td>
</tr>
<tr>
<td>WS</td>
<td>Wind stress</td>
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1. Introduction

One of the most important scientific topics of our time concerns climate change due to human emissions of carbon dioxide (CO$_2$), and its potential consequences for planet Earth and for humanity (IPCC, 2014, 2019). To understand the effect of CO$_2$ emissions on climate, we need to understand the processes of Earth’s carbon cycle that transfer carbon between different reservoirs. Human activity releases excess CO$_2$ into the atmosphere, but the atmosphere interacts with for example vegetation on land, and with the sea surface. Because of these interactions, some of this carbon is transferred to the terrestrial and oceanic carbon reservoirs (Figure 1.1).

The oceanic reservoir of carbon is vast, and much larger than its atmospheric and terrestrial counterparts—when adding these three carbon reservoirs, the ocean contains more than 90% of the total amount of carbon (Ciais et al., 2013, Heinze et al., 2015). Since the start of the industrial era, it is estimated that roughly 30% of anthropogenic emissions of CO$_2$ have been taken up and stored in the ocean (DeVries, 2014, Gruber et al., 2019, Sabine et al., 2004). However, the question whether the oceanic sink for CO$_2$ will remain as strong in the future remains open (Gruber et al., 2019, Le Quéré et al., 2007). A large body of research also indicates that the low atmospheric CO$_2$ in glacial periods, which has been recorded in ice cores (Lüthi et al., 2008, Petit et al., 1999), was primarily caused by increased storage of carbon in the ocean reservoir (studied and reviewed by e.g., Broecker, 1982, Kohfeld & Ridgwell, 2009, Sigman & Boyle, 2000). Yet, state of the art climate models struggle to reproduce this transfer of carbon from the atmosphere to the ocean.

Across climate states, changes in ocean temperature (Broecker, 1982, De Boer et al., 2007, Watson et al., 2015), circulation (Sarmiento & Toggweiler, 1984), stratification (Ballarotta et al., 2014), mixing (Watson & Naveira Garabato, 2006), and biological and chemical processes (Broecker, 1982, Martin, 1990, Sigman & Boyle, 2000) can cause changes in ocean carbon storage. All of these processes likely played a role for glacial–interglacial changes in atmospheric CO$_2$ (Ballarotta et al., 2014, Bouttes et al., 2011, Broecker, 1982, Brovkin et al., 2007, De Boer et al., 2007, Kohfeld & Chase, 2017, Kohfeld & Ridgwell, 2009, Marinov et al., 2008, Sigman & Boyle, 2000, Watson et al., 2000). In order to predict the response of the ocean carbon storage to future climate change, we need to understand the sensitivity of the processes involved, and we need to understand how these processes have responded in climate scenarios that we have data records from. This thesis aims to contribute to this understanding, and to improve our ability to simulate these processes with climate models. To this end, we use model simulations and climate data records.

Direct observations of ocean properties are still sparse, both in time and space, but new technology such as autonomous floats (Argo, 2019) and satellites are continuously increasing the available information. For analysis of the modern–day ocean...
Figure 1.1: Simplified illustration of the global carbon cycle as shown in Heinze et al. (2015), and originally adapted from Ciais et al. (2013). Caption as per Heinze et al. (2015), Fig. 6: ‘Reservoir mass numbers and annual exchange fluxes are given in PgC ($10^{15}$ gC) and PgC yr$^{-1}$, respectively. Black numbers refer to pre–industrial values (before 1750). Red flux numbers represent annual anthropogenic fluxes averaged over the years 2000–2009 and red reservoir numbers depict cumulative changes of anthropogenic carbon between 1750 and 2011 (90% confidence interval). A positive cumulative change denotes an increase in (gain of) carbon since the onset of the Industrial Era. Land–atmosphere carbon fluxes caused by rock weathering, volcanism and freshwater outgassing amount in total to a flux of 0.8 PgC yr$^{-1}$ and are represented by the green number. Purely land–based processes like further rock weathering, burial and export from soils to rivers are not depicted in the scheme above. The star (*) indicates that the given accumulation number refers to a combined value for Surface Ocean and Intermediate and Deep Ocean.’

state, data products with gridded and time–averaged representations of the available data, such as the World Ocean Atlas (e.g., Locarnini et al., 2018) and GLODAP (Olsen et al., 2016), are frequently used.

To get information about Earth’s climate and the ocean state in periods in Earth’s history, we need to use indirect observations, also called proxy data. A wide range of climate proxies such as isotope tracers are used to understand paleoclimate from archives including ice (Headly & Severinghaus, 2007), sediment cores (Kohfeld et al., 2013, Oliver et al., 2010, Peterson et al., 2014), corals (Robinson et al., 2014), and pollen fossils (Crowley, 1995). For the Last Glacial Maximum (LGM, $\sim$ 19–23 ka),
such paleorecords have been widely used (exemplified by some important studies), to get information about atmosphere and ocean characteristics, such as wind- and precipitation patterns (Kohfeld et al., 2013, Sime et al., 2013), dust deposition (Kohfeld et al., 2013, Mahowald et al., 2006), ocean temperature (Bereiter et al., 2018, Headly & Severinghaus, 2007), water mass distribution and ocean circulation (Broecker, 1998, Curry & Oppo, 2005, Matsumoto, 2007b), export of organic matter from the surface ocean to the deep (Kohfeld et al., 2013), carbon storage on land and in the ocean (Peterson et al., 2014) etc. Through the information obtained from these proxy records, numerical climate models can then help us simulate paleoclimate in response to reasonably well-known forcings. Model performance can also be tested against these records (Bouttes et al., 2011, Brovkin et al., 2007, Menviel et al., 2012, Muglia et al., 2018, Sime et al., 2013). Such tests can help us assess the accuracy of models that are used for simulations of future scenarios. Conversely, the models can help us extrapolate and interpolate proxy records, and to interpret them.

This thesis focuses on the naturally occurring processes involved in ocean carbon storage, and transport, and on numerical model analysis of these processes. In the included studies, we use observational as well as proxy records of oceanic properties to evaluate our model simulations. The thesis contributes to the general understanding of the interplay between ocean circulation and ocean carbon storage in model simulations, and of the importance of the initial state and model parameterisations for the simulated ocean carbon storage. It adds specifically to the understanding of glacial model simulations, contributes a new representation of oceanic $\delta^{13}C$ records, and proposes a new method for analysis of meridional ocean carbon transport.

The thesis is organised as follows. Chapter 2 gives an introduction to paleoclimate studies, and particularly to glacial–interglacial cycles. In Chapter 3, climate models are introduced, and modelling strategies are explained. Chapter 4 provides concepts for studies of the ocean carbon cycle, the processes involved in ocean carbon storage, and the use of carbon isotopes as indicators for ocean circulation and carbon storage. In this chapter, the main findings of Papers I–III are also presented. Chapter 5 introduces Paper IV and some applications of its streamfunction–based method for analysis of meridional ocean carbon transport. Chapter 6 concludes the results of the thesis, and provides an outlook. Papers I–IV are provided as separate chapters after the executive summary.
2. Paleoclimate

2.1 What can we learn from studying historical climate regimes?

The study of climate regimes in Earth’s geological past (paleoclimate) can provide important insights to the response of physical and biogeochemical processes to climate changes. It can help us constrain the variability of important climate system components, such as atmospheric CO$_2$, atmospheric- and ocean circulation, ice sheets and sea–ice, marine productivity, and more. It can also help us understand feedbacks in the climate system, especially on time scales that are longer than our observational data records (Masson-Delmotte et al., 2013). In addition, paleoclimate studies help to validate and constrain climate model simulations, and to evaluate the model response to known forcings, as we demonstrate in this thesis.

2.2 Glacial vs. interglacial climate

In this thesis, we run and analyse model simulations of interglacial/pre–industrial/modern (Papers I–IV), as well as glacial–like (Papers II–III), climate. This section provides some background to how interglacial and glacial climate differ from each other.

Glacial–interglacial cycles occur mainly as a result of variations in Earth’s orbital parameters, which influence the amount of incoming solar radiation. However, atmospheric CO$_2$ provides an important feedback for these cycles, and contributes a lot of the observed climate variability (Masson-Delmotte et al., 2013, and references therein). For glacial inception to occur, the Northern Hemisphere incoming summer solar radiation and the atmospheric CO$_2$ concentration both need to be low enough (Ganopolski et al., 2016). During glacial periods, atmospheric CO$_2$ is further reduced compared to interglacials by $\sim 90 - 100$ ppm (Lüthi et al., 2008, Petit et al., 1999). As a result, glacial periods are substantially colder than interglacials – the LGM global mean surface air temperature is estimated to have been 3–8 °C colder than the pre–industrial (i.e. before anthropogenic warming started) (IPCC, 2014), while global mean sea–surface temperature and the global ocean mean temperature are estimated to have been 0.7–2.7 °C (Members et al., 2009) and 2.0–3.2 °C (Bereiter et al., 2018, Headly & Severinghaus, 2007) colder, respectively. A colder ocean can hold more carbon, due to the temperature effect on solubility (see Section 4.1). A colder climate is also drier, and the dry conditions led to increased dust deposition compared to interglacial climate (Mahowald et al., 2006). Dust is rich in bio–available iron, and it
has been hypothesised that the increased iron–availability strengthened the biological sequestration of carbon in the glacial ocean compared to interglacials (Martin, 1990).

At the LGM, ice–sheets covered large parts of Scandinavia and North America (Clark et al., 2009). As a result, sea–level was approximately 130 m lower (Clark et al., 2009, Simms et al., 2019), more of the continental shelves were exposed and coastlines were displaced compared to modern–day (Huybrechts, 2002). As large volumes of freshwater were stored in ice, ocean salinity was higher than today (Sigman & Boyle, 2000). Sea–ice cover was also greater than today, and expanded equatorward (Fig. 2.1).

Proxy records from the ocean indicate that the glacial Atlantic meridional overturning circulation (AMOC) pattern and water mass distribution was different (Hesse et al., 2011, Kohfeld & Chase, 2017, Lynch-Stieglitz et al., 2007) from today. This is illustrated in Figure 2.1, reproduced from Kohfeld & Chase (2017). The Antarctic Bottom Water, which forms and sinks around the Antarctic margin, occupied a larger volume, but was ventilated at a slower rate compared to today. Consequently, the North Atlantic Deepwater (NADW), which forms in the North Atlantic and the Nordic Seas, was confined to shallower depths. Model simulations disagree on the strength of the glacial AMOC, and some suggest the NADW was circulating at a faster rate than today (Otto-Bliesner et al., 2007), while the proxy records indicate that the glacial AMOC was similar in strength or weaker than today. Thus, with the help of the proxy data, we can rule out the simulations that do not represent the glacial ocean state (Lynch-Stieglitz et al., 2007). The proxy records also indicate that terrestrial carbon storage was lower in the LGM compared to the current interglacial period (the Holocene, Jeltsch-Thömmes et al., 2019, Peterson et al., 2014, Shackleton, 1977).

It is hypothesised that the weak ventilation, and the increased stratification, of the glacial deep ocean led to more carbon being trapped there, thus contributing to the low glacial atmospheric CO$_2$ (Kohfeld & Chase, 2017, Sigman & Boyle, 2000). Weaker upwelling in the Southern Ocean, in combination with expanded sea–ice (winter) and surface stratification due to sea–ice melt (summer), may have reduced air–sea gas exchange and led to weaker out–gassing of excess CO$_2$ from the deep ocean. For ocean microorganisms that capture carbon through photosynthesis, a weak overturning means a weaker supply of nutrients necessary for carbon capture, but a long residence time at the surface and more time to use the available nutrients. The reinforcement of biological carbon capture caused by long residence time and increased iron supply, seems to outcompete the negative effect of reduced upwelling of nutrients, and makes the ocean’s so called “biological pump” stronger (see Section 4.2). The connection between overturning strength and ocean carbon storage is more extensively discussed in Section 4.3.
Figure 2.1: Schematic figure from Kohfeld & Chase (2017), showing the Atlantic Ocean overturning circulation pattern in interglacial periods (top panel, a) and glacial periods (bottom panel, c). The top panel schematic is drawn for interglacial stage 5E (118–127 ka), but is also representative of modern–day circulation. The bottom panel is drawn to represent glacial stage 4 (59–68 ka), which is before, but expected to be similar to, the LGM. The curve in the bottom right corner of each panel shows the atmospheric CO$_2$ curve of Jouzel et al. (2007) from 0–150 ka, and the arrows indicate the positions of the stages 5E and 4, respectively. Note that the middle panel (b) of the original publication has been left out, as it represents an intermediate circulation state not relevant for this text. Abbreviations AABW, NADW and GNADW represent Antarctic Bottom Water, North Atlantic Deepwater and Glacial North Atlantic Deepwater, respectively.
3. Climate modelling

Numerical models that simulate the processes of the Earth system are important tools for learning about climate and the carbon cycle. With these models, we can learn about which processes are necessary to represent historical climate changes, and which processes may become important in future climate scenarios. Climate models generally simulate the dynamics of the Earth’s atmosphere and oceans, sometimes with interactive land surface, sea–ice, ice sheets etc. (IPCC, 2014). Many models also simulate the carbon system, some only for the atmosphere and oceans (atmospheric chemistry and ocean biogeochemistry), and some also for additional carbon reservoirs in e.g. terrestrial vegetation, soil, ocean sediments (IPCC, 2014).

For the studies in this thesis, we use two different climate models with different levels of complexity. The resolutions of these two models are compared in Table 3.1. In Papers I, II, and III, we use the model cGENIE (cGENIE release v0.9.5, 2019, Ridgwell et al., 2007), which is a so called “Earth System model of Intermediate Complexity” (EMIC). This type of model is more complex than a box model, which represents the ocean and atmosphere with only a few homogeneous boxes, but is less complex than a general circulation model (GCM). cGENIE represents the ocean by a 3D grid, but with low resolution and simplified physics for ocean circulation. It uses a simplified energy–moisture balance models for the atmosphere, where atmospheric dynamics are 2D, and prescribed rather than interactive (i.e. they do not change in response to changes in climate). cGENIE uses interactive atmospheric chemistry and ocean biogeochemistry. The ocean biogeochemical module allows for simulation of an unusually large number of ocean tracers (Table 3.1). The reduced complexity in resolution and physics allows for high computational efficiency, even with high complexity in the representation of biogeochemical processes and tracers. This makes EMICs like cGENIE suitable for studies that require simulations that span long time periods (many millenia) or a large number of simulations.

In Paper IV, we use a GCM called NEMO–MEDUSA (Yool et al., 2013, 2015), which is a fully coupled physical–biogeochemical model, with higher resolution and more complex physics than cGENIE, but with fewer biogeochemical tracers (see Table 3.1). Such high–resolution models require more computational capacity. They are therefore more suitable for simulations of shorter time periods, and of the modern day climate system where higher–resolution observations are available for model–data comparison.

3.1 Steady state vs. transient simulations

When modelling the climate system, we either aim to simulate a climate state (steady), or the evolution (transient) of the climate over some time period.
Table 3.1: Resolution comparison of the two models cGENIE (Papers I, II, and III, and cGENIE release v0.9.5, 2019, Ridgwell et al., 2007) and NEMO-MEDUSA (Paper IV, and Yool et al., 2013, 2015).

<table>
<thead>
<tr>
<th>Resolution</th>
<th>cGENIE</th>
<th>NEMO–MEDUSA</th>
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</thead>
<tbody>
<tr>
<td>Atm. dynamics</td>
<td>prescribed</td>
<td>interactive</td>
</tr>
<tr>
<td>Atm. chemistry</td>
<td>interactive</td>
<td>interactive</td>
</tr>
<tr>
<td>Ocn. horizontal grid</td>
<td>$36 \times 36$ equal area cells</td>
<td>$\sim 1/4^\circ$</td>
</tr>
<tr>
<td></td>
<td>($\sim 10^\circ$ at equator)</td>
<td></td>
</tr>
<tr>
<td>Ocn. vertical grid</td>
<td>16 levels</td>
<td>75 levels</td>
</tr>
<tr>
<td>Ocean tracers</td>
<td>101</td>
<td>15</td>
</tr>
<tr>
<td>and state variables</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In a steady state simulation, we apply appropriate boundary conditions and forcings, such as land–sea mask, atmospheric CO$_2$, and orbital forcing, to represent a specific climate state, and allow the model to evolve until its dynamics and chemical characteristics stabilise. This method is used in Papers I, II, and III.

In a transient simulation, some forcings (for example atmospheric CO$_2$), and thus the climate, evolve over time. This type of simulations allows us to represent a historical period, which can be useful for comparison with observational time series, or future scenarios, where the gradual changes of the climate system and its processes are of interest. In Paper IV, we use a transient simulation representative of the industrial era. As we want to analyse the modern ocean, which is subject to forcing from anthropogenic CO$_2$, a transient simulation is likely to achieve a more accurate representation of the modern ocean state compared to a steady state simulation.

3.2 Ensemble simulations

An ensemble of simulations is usually a suite of similar simulations designed to investigate how sensitive a model is to changes in boundary conditions, forcings, or model parameters. This is common practice in model studies of paleo- (e.g., Bouttes et al., 2011, Galbraith & de Lavergne, 2018, Klockmann et al., 2016, Marinov et al., 2008, Menviel et al., 2012), as well as future climate (de Lavergne et al., 2014, DeConto & Pollard, 2016, Knutti et al., 2002). Model sensitivity studies of this kind can for example be used to draw conclusions about the importance of individual physical or chemical processes, which is the case in Papers I and II, or to find the best model representation of observations, which is the case in Paper III, and to determine the uncertainty of model simulations. This type of ensemble simulation scheme is exemplified in Figure 3.1 by the ensemble we created for Paper I. The scheme begins with a spin–up (top grey box) to reach a control state (blue box). From the control state, we run experiments where we change for example the wind stress, or the ocean mixing (middle grey box), which results in an ensemble of simulations (orange box). In the next step, we run a biological experiment (bottom grey box) starting from the orange ensemble, which results in a second ensemble of simulations (red box). The results of these ensemble simulations are discussed in Section 4.3.1.
Ensembles can also consist of similar experiments run with different models, in order to perform a model–intercomparison study (e.g., Taylor et al., 2012). Multi-model ensembles are for example used to determine the range of uncertainty of the results presented in the IPCC reports (IPCC, 2007, 2014), for evaluating the level of agreement regarding future and paleoclimate circulation patterns (e.g., Braconnot et al., 2007, Muglia & Schmittner, 2015, Otto-Bliesner et al., 2007, Weaver et al., 2012, Weber et al., 2007), and for assessing how to improve model comparability (e.g., Marzocchi & Jansen, 2017, Séférian et al., 2016, Weber et al., 2007).

Figure 3.1: Ensemble generation scheme for Paper I. Each large box corresponds to a step in the simulation process, and each small numbered box corresponds to a resulting ensemble member. The process begins with a spin–up (top grey box) leading to a control state (blue box). From the blue control state, 12 simulations are run where physical parameters have been changed, which results in 12 new states (orange ensemble members, described further in Table 4.1). From the orange ensemble members, we run a second experiment, resulting in 12 more ensemble members. This second experiment is also run for the blue control state, which results in a red control experiment. The blue box is the control state to which the orange ensemble members are compared, and the red box is the control state for the purple ensemble members.
4. The ocean carbon pumps

Carbon enters the ocean reservoir by exchange with the atmosphere and through input from land sources via rivers (Figure 1.1). Both of these sources of carbon are located at the ocean surface, so how does carbon reach the deep ocean? Some carbon enters the deep ocean via deep water formation. The carbon concentration held in the water when it subducts is retained and advected along with the water as it flows through the deep ocean. This process is referred to as the solubility pump (Section 4.1). Some carbon is taken up by photosynthetic organisms in the surface ocean. When these organisms die, some of them fall out of the surface layer and reach deeper waters, where they are decomposed and the carbon comes back into the water mass. This process is called the biological pump (Section 4.2). Together, these pumps act to keep carbon in the ocean interior, and away from the atmosphere.

4.1 The solubility pump

$CO_2$ is transferred from the atmosphere to the surface ocean by dissolution. The gas dissolves in the water, and then partly reacts with the water to form carbon acid ($H_2CO_3$, Eq. 4.1), which in turn dissociates to bicarbonate ($HCO_3^-$, Eq. 4.2) and carbonate ($CO_3^{2-}$, Eq. 4.3) ions.

\[
\begin{align*}
CO_2(aq) + H_2O & \rightleftharpoons H_2CO_3 \quad (4.1) \\
H_2CO_3 & \rightleftharpoons H^+ + HCO_3^- \quad (4.2) \\
HCO_3^- & \rightleftharpoons H^+ + CO_3^{2-} \quad (4.3)
\end{align*}
\]

In the ocean, about 90% of the dissolved $CO_2$ exists as bicarbonate, and 9% as carbonate (Williams & Follows, 2011), while the concentrations of aqueous $CO_2$ and carbonic acid are very small. Together, these species are referred to as dissolved inorganic carbon (DIC). The water temperature and alkalinity, as well as the partial pressure of $CO_2$ in the overlying atmosphere, will determine the saturation concentration of DIC in a water parcel. We will henceforth refer to this concentration as “saturation carbon”, or $C_{sat}$. The fact that $CO_2$, unlike for example $O_2$, reacts with the water, causes air–sea gas exchange of $CO_2$ to be about 10 times slower than for non–reactive gases. The characteristic time scale for air–sea equilibration is $\sim 1$ year for $CO_2$ compared to $\sim 1$ month for a non–reactive gas (Williams & Follows, 2011). It is therefore difficult for the surface water to equilibrate with the atmosphere before being subducted again, and a water parcel will often be over- or under saturated in $CO_2$. This offset, or disequilibrium, will henceforth be referred to as “disequilibrium.
carbon”, or $C_{dis}$, and can be either a positive, or a negative concentration. DIC in the form of $C_{sat}$ and $C_{dis}$, also known as preformed carbon ($C_{pre} = C_{sat} + C_{dis}$), can then be transferred to the deep ocean through subduction when deep water is formed. This process is known as “the solubility pump” (Volk & Hoffert, 1985). For a schematic image of the solubility pump, see the right hand side of Figure 4.1. The full carbon separation framework is described in Section 4.3.

Figure 4.1: Schematic image showing the carbon species associated with the biological and the solubility pump, respectively. The full carbon separation framework is described in Section 4.3.

4.2 The biological pump

Photosynthetic microorganisms (phytoplankton) in the surface ocean capture CO$_2$ and bind it in their tissue. When these organisms die and fall out of the surface ocean, or are subducted along with a water parcel, this organic carbon is exported to the interior ocean where it is remineralised back into DIC. This fraction of DIC is referred to as “soft tissue carbon”, or $C_{soft}$. Some of the phytoplankton also form carbonate shells. These shells dissolve at depth, and the DIC associated with this dissolution will be referred to as $C_{carb}$, or “hard tissue carbon”. Together, we refer to the two biologically–sourced DIC species as regenerated carbon ($C_{reg} = C_{soft} + C_{carb}$). The term commonly used to describe the transfer of biologically sourced carbon to the ocean interior is “the biological pump” (Volk & Hoffert, 1985). The biological pump
is shown on the left hand side of Figure 4.1. It should be noted that, when carbonate is taken up in the surface ocean this acts to decrease atmospheric CO$_2$. However, the carbonate uptake is associated with an uptake of alkalinity, which is twice as large and acts to increase CO$_2$ through reduced solubility. The net effect of carbonate uptake is therefore a decrease of 2 mol in $C_{\text{sat}}$ for each mol of $C_{\text{carb}}$, a release of 1 mol CO$_2$ to the atmosphere, and reduced ocean carbon storage. This is sometimes referred to as “the carbonate counter pump” (Kohfeld & Ridgwell, 2009).

4.3 Carbon separation framework

From the descriptions of the solubility pump (Section 4.1), and the biological pump (Section 4.2), we can infer a carbon separation framework (Ito & Follows, 2005) which partitions the total ocean DIC concentration ($C_{\text{tot}}$) into contributions from dominant ocean processes.

$$C_{\text{tot}} = C_{\text{sat}} + C_{\text{dis}} + C_{\text{soft}} + C_{\text{carb}}$$ (4.4)

As seen in Figure 4.1, the two species of DIC that are associated with the solubility pump ($C_{\text{sat}}$ and $C_{\text{dis}}$) are together referred to as preformed carbon ($C_{\text{pre}}$), as these are present in the water before downwelling, and then passively transported and mixed in the interior ocean. $C_{\text{soft}}$ and $C_{\text{carb}}$, associated with the biological pump, are referred to as regenerated carbon ($C_{\text{reg}}$), as this form of DIC appears in the interior ocean when biologically sourced material is regenerated to DIC.

In this thesis, we use this carbon separation framework (Paper I, Section 3.2; Paper II, Section 2.5; Paper IV, Section 2.1) to draw conclusions about the processes involved in ocean carbon storage, and how these respond to changes in climate and ocean circulation.

4.3.1 Paper I

In Paper I, we apply the carbon separation framework to the example ensemble in Figure 3.1. The ensemble explores changes in atmospheric heat diffusivity ($AD$), wind stress ($WS$), diapycnal ($DD$, vertical) and isopycnal ($ID$, horizontal) diffusivity with respect to a pre–industrial control state (PIES278) (Table 4.1). This analysis reveals that differences in ocean carbon storage between ensemble members are often dominated by differences in the strength of the biological pump (Fig. 4.2, blue bars in panels a and c, where panel a is the composite of panels b–d). In Figure 4.2, pale pink bars (panel b) compared to pale blue bars (panel c) illustrate the carbonate counter pump – a change in $C_{\text{carb}}$ compared to the control state is counteracted by a larger change in $C_{\text{sat}}$ that originates from the change in surface alkalinity. Changes in $C_{\text{dis}}$ (the main contributor to yellow bars in panels a and d) are often minor, but there is an interesting exception: the simulation $AD/2$, with halved atmospheric heat diffusivity compared to the control state. In $AD/2$, the change in $C_{\text{soft}}$ is almost entirely counteracted by a change in $C_{\text{dis}}$. In Paper I, we conclude that this large change in $C_{\text{dis}}$ is likely due to the large expansion of sea–ice cover in this simulation compared to the pre–industrial
Table 4.1: List of sensitivity experiment equilibrium states SE1–SE12 (Figure 3.1, abbreviated ensemble member description, and specification of which one or two physical characteristics have been altered compared to the pre–industrial control state (PIES278). The nature of the change is specified within parenthesis. Note that this table corresponds to the corrected version in the Corrigendum for Paper I.

<table>
<thead>
<tr>
<th>Ensemble member</th>
<th>Abbreviated member description</th>
<th>Adjusted parameter (adjustment)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SE1</td>
<td>‘WS×2’</td>
<td>Wind stress intensity (doubled)</td>
</tr>
<tr>
<td>SE2</td>
<td>‘WS/2’</td>
<td>Wind stress intensity (halved)</td>
</tr>
<tr>
<td>SE3</td>
<td>‘AD×2’</td>
<td>Atmospheric heat diffusivity (doubled)</td>
</tr>
<tr>
<td>SE4</td>
<td>‘AD/2’</td>
<td>Atmospheric heat diffusivity (halved)</td>
</tr>
<tr>
<td>SE5</td>
<td>‘DD×2’</td>
<td>Ocean diapycnal diffusivity (doubled)</td>
</tr>
<tr>
<td>SE6</td>
<td>‘DD/2’</td>
<td>Ocean diapycnal diffusivity (halved)</td>
</tr>
<tr>
<td>SE7</td>
<td>‘ID×2’</td>
<td>Ocean isopycnal diffusivity (doubled)</td>
</tr>
<tr>
<td>SE8</td>
<td>‘ID/2’</td>
<td>Ocean isopycnal diffusivity (halved)</td>
</tr>
<tr>
<td>SE9</td>
<td>‘WS/2_DD/2’</td>
<td>Wind stress intensity (halved) and ocean diapycnal diffusivity (halved)</td>
</tr>
<tr>
<td>SE10</td>
<td>‘AD×2_DD×2’</td>
<td>Atmospheric heat diffusivity (doubled) and ocean diapycnal diffusivity (doubled)</td>
</tr>
<tr>
<td>SE11</td>
<td>‘DD×2_ID×2’</td>
<td>Ocean diapycnal diffusivity (doubled), and isopycnal diffusivity (doubled)</td>
</tr>
<tr>
<td>SE12</td>
<td>‘DD/2_ID×2’</td>
<td>Ocean diapycnal diffusivity (halved), and isopycnal diffusivity (doubled)</td>
</tr>
</tbody>
</table>

This result is interesting from the perspective of glacial–interglacial cycles, when sea–ice cover was much more extensive than in the pre–industrial climate.

Another key result from Paper I is the close connection between the ocean carbon storage and the net strength of the global overturning circulation (OVT, Figure 4.3), where stronger overturning means less carbon is stored in the global ocean. The carbon separation framework reveals that the strength of the overturning circulation affects the ocean carbon cycle in several ways. In our ensemble, members with a stronger overturning tend to have a warmer global ocean, primarily due to a deeper mixed layer. Thus, stronger OVT leads to less $C_{sat}$.

Another important factor is the overturning time scale in relationship to the carbon cycle time scales. For the biological pump, stronger overturning leaves less time for efficient use of nutrients at the ocean surface before the water is subducted. Thus stronger OVT is associated with a weaker biological pump (Fig. 4.3, left panel). In our experiments, this effect on $C_{sof}$, and the temperature effect on $C_{sat}$, are the most important processes for the correlation between OVT and ocean carbon storage. In addition, the relationship between the overturning time scale and the air–sea gas exchange time scale is of importance for the disequilibrium component of the solubility pump.

In the North Atlantic, warm water is carried northward by the currents and cooling along its path (Fig. 2.1). Colder water can hold more dissolved CO$_2$, but as discussed
Figure 4.2: Observed changes in total model atmosphere–ocean carbon inventory ($\Delta TC$) for SE1–SE12 (Figure 3.1) compared to the total carbon inventory of the control pre–industrial state (PIES278). Note that in this case, the atmosphere is restored to maintain the same CO$_2$ concentration across all simulations, thus $\Delta TC$ consists exclusively of changes in the model ocean carbon inventory. In panel (a), green bars show $\Delta TC$, while other bars show relative contributions to $\Delta TC$ by changes in the solubility ($C_{\text{sat}}$, due to temperature in red, due to preformed alkalinity in pink; panels a, b), biological soft–tissue ($C_{\text{soft}}$, dark blue, panels a, c) and carbonate–tissue ($C_{\text{carb}}$, light blue, panels a, c) pumps. The residual of the theoretical contributions by changes in $C_{\text{soft}}$, $C_{\text{carb}}$ and $C_{\text{sat}}$ to $\Delta TC$ and the observed model $\Delta TC$ is denoted $C_{\text{res}}$ (yellow bars, panels a, d). The main contributor to the observed residual $C_{\text{res}}$ is disequilibrium carbon ($C_{\text{dis}}$). The horizontal axis shows the magnitude of changes given in 10$^{16}$ mol ($\sim$ 120 Pg C). Note that an inconsistency in the configuration files for the simulation WS/2 was discovered after publication of this figure (see Paper I, Corrigendum). This individual simulation should not be included in detailed analysis of this figure.
in Section 4.1, air–sea gas exchange for CO₂ is slow. If the overturning is strong, water may be subducted before the equilibrium concentration has been reached, thus leaving the North Atlantic deep water under–saturated in CO₂ (i.e. $C_{\text{dis}} < 0$).

In the Southern Ocean, deep waters rich in accumulated $C_{\text{bio}}$ upwell to the surface. When overturning is strong, these waters will still be over–saturated at the time of subduction (i.e. $C_{\text{dis}} > 0$). The effects of overturning time scale on $C_{\text{dis}}$ in the Northern and Southern Hemispheres compete with each other, as well as with effects of changes in sea–ice cover, and the effect of OVT on $C_{\text{dis}}$ is therefore less straightforward. Similar results linking ocean storage of $C_{\text{soft}}$ and $C_{\text{dis}}$ to ocean ventilation have been found by Eggleston & Galbraith (2018). Our results show that this link exists also for $C_{\text{sat}}$, and, more importantly, for the total ocean carbon storage (TC), which is more strongly correlated with OVT than any of the individual carbon components are (Figure 4.3, right panel).

In addition, our second step ensemble simulations (Figure 3.1, purple box) reveal that the initial state ocean carbon inventory determines the response in atmospheric CO₂ to a perturbation that maximises the efficiency of the ocean biology.

### 4.4 Nutrients and stoichiometry

Photosynthesis also requires nutrients such as phosphorus (P) and nitrogen (N). When organic matter is exported to the ocean interior, nutrients are exported together with the organic carbon. In the same way as carbon, these are regenerated to dissolved inorganic nutrients in the ocean interior. Redfield et al. (1963) showed that the elemental composition (stoichiometry) of marine microorganisms and the ratios of inorganic nutrients ($PO_4$, $NO_3$) to DIC in the ocean interior are strikingly similar. In addition, regeneration of organic molecules requires a certain amount of oxygen. The classical Redfield ratios are $P:N:C:O_2 = 1:16:106:138$. In later years, studies based on a larger number of observations have suggested adjustments to the Redfield ratios, and even
though the classical Redfield ratios are still used in many applications, the updated estimate of Anderson & Sarmiento (1994) (P:N:C:O$_2$ = 1:16±1:117±14:-170±10) is sometimes preferred.

![Figure 4.4: Flexible stoichiometry C/P (y-axis) dependent on the PO$_4$-concentration [µmolL$^{-1}$] (x-axis), as described by Eq. 1. Here, we extend the relationship beyond the observational interval 0–1.7 µmolL$^{-1}$ (bounded by dashed line) which form the basis of the relation derived by Galbraith & Martiny (2015).](image)

When nutrients are abundant, fixed ratios can be a good approximation. However, when nutrients are scarce, the phytoplankton community has been shown to adapt to the low nutrient conditions, both by adjusting the species composition and by individual organisms being more frugal with nutrients (Galbraith & Martiny, 2015, and references therein). Martiny et al. (2013) showed that the elemental ratios vary regionally, and latitudinally. These variations were mainly attributed to differences in species composition between regions resulting from differences in nutrient availability and temperature, where warm and nutrient poor areas are associated with high ratios of C/P and N/P, while cold and nutrient rich waters show lower ratios. Based on observations, Galbraith & Martiny (2015) suggested that the local C/P ratio can be predicted from water PO$_4$–concentration (Figure 4.4), through

$$P : C = 1 : \left(\frac{[PO_4]}{144.9 \mu molL^{-1}} + 0.0060\right)^{-1}. \quad (4.5)$$

4.4.1 Paper II

In Paper II, we use this as a parameterisation of the C/P composition of organic matter produced by photosynthetic organisms in the surface layer. We compare the results of simulations that use this parameterisation to results of the similar simulations using constant Redfield C/P compositon. From this, we conclude that the choice of
parameterisation can have major implications for the result of e.g. attempts to simulate glacial–interglacial cycles in atmospheric CO\textsubscript{2}. In our simulations which combined several glacial–like forcings, p\textsubscript{CO\textsubscript{2}}\textsubscript{atm} was strongly reduced compared to the pre–industrial control (Ctrl) when using Redfield C/P composition (-64 ppm). However, the reduction was 25% larger for the flexible C/P parameterisation (-80 ppm), and came closer to the $\sim -90$ ppm suggested by proxy records for the LGM p\textsubscript{CO\textsubscript{2}}\textsubscript{atm} (Lüthi et al., 2008, Petit et al., 1999).

In our glacial–like simulations, the biological pump becomes stronger compared to Ctrl, both with Redfield (RED) and flexible C/P (GAM) composition, but the effect is more pronounced in GAM. This can be explained by an offset between changes in regenerated nutrients ($P_{\text{reg}}$) and regenerated carbon ($C_{\text{reg}}$, Section 4.3). As the climate cools, biological production slows down and export of carbon to the deep ocean is reduced. However, the cooler climate also leads to increased retention of carbon in the deep ocean, through deeper remineralisation (Matsumoto, 2007a), and increased residence time of the AABW (Section 2.2). Due to the competing effects between reduced export and increased retention, the change in $P_{\text{reg}}$ is small between our control and glacial—like state. In RED, where C/P is fixed, the increase in $C_{\text{reg}}$ is tied in fixed proportions to the small increase in $P_{\text{reg}}$. In GAM, C/P responds to changes in surface nutrient fields, and $C_{\text{reg}}$ increases while maintaining, or even decreasing, the fraction of regenerated to total nutrients in the deep ocean.

4.5 $\delta^{13}$C as a proxy for ocean circulation and carbon storage

Ocean carbon storage varies both in space and time. Carbon is redistributed by ocean currents, and mixing between water masses, and by sinking of biogenic material that is regenerated to inorganic carbon at depth. Carbon atoms occur naturally as three different isotopes, $^{12}$C, $^{13}$C, and $^{14}$C, out of which $^{12}$C is by far the most common ($\sim 99\%$). $^{12}$C and $^{13}$C are stable, while $^{14}$C (radiocarbon) undergoes radioactive decay. $^{14}$C is often used in paleoclimate studies as a means of determining age, of samples as well as water masses (e.g., Matsumoto, 2007b). In this thesis, however, we use the stable isotope ratio of $^{13}$C/$^{12}$C.

$\delta^{13}$C is a measure of how the ratio in a sample, $R_{\text{sam}} = ^{13}$C/$^{12}$C, compares to a standard reference value, $R_{\text{ref}}$, commonly the Vienna PeeDee Belemnite (V.P.D.B. or PDB). A sample that is enriched in $^{13}$C compared to the standard reference, will have $\delta^{13}$C > 0, while a depleted sample will have $\delta^{13}$C < 0 (Eq. 4.6). Variations are small, and $\delta^{13}$C is measured in parts per thousand (‰).

$$\delta^{13}$C(‰) = \left(\frac{R_{\text{sam}}}{R_{\text{ref}}} - 1\right) \times 10^3 \quad \text{(4.6)}$$

In paleoceanography, $\delta^{13}$C is usually measured from fossils of microorganisms with calcium carbonate shells such as foraminifera. While they were alive, these organisms recorded the isotopic signature of the surrounding water mass in their shells, either in the upper ocean (planktic foraminifera), or on/near the ocean floor (benthic
foraminifera). By determining the species and the age of the fossil, paleoceanographers can approximate the $\delta^{13}C$ of the ocean region and water–mass they lived in. In their review of $\delta^{13}C$ in paleoceanography studies, Mackensen & Schmiedl (2019) show that this fact has made it a powerful tool for learning about ocean circulation, deep–water ventilation, and ocean biological productivity in past climate states.

As described in the following paragraphs, ocean $\delta^{13}C$ is influenced by a number of processes, such as air–sea gas exchange, biological production/decomposition, and ocean circulation and mixing (see reviews by Mackensen & Schmiedl, 2019, Peterson et al., 2014, Schmittner et al., 2013, and references therein).

Air–sea exchange of CO$_2$ is influenced by temperature, which leads to increased $\delta^{13}C$ in cold water, and decreased $\delta^{13}C$ in warm water. Photosynthetic organisms, in the ocean as well as on land, preferentially take up $^{12}C$, and are therefore strongly depleted in $\delta^{13}C$ compared to their surroundings. The typical $\delta^{13}C$ of plankton in the surface ocean is ~-21‰ compared to the surface water average of +2‰. As a consequence, photosynthesis enriches the surface ocean in $\delta^{13}C$, but in the deep ocean, the remineralisation of dead material will release this depleted carbon back into the water (i.e., $C_{sof}$ has a depleted $\delta^{13}C$ signature). The biological pump therefore contributes to a vertical gradient in $\delta^{13}C$ in the ocean. However, as mentioned above, in the calcareous shells of foraminifera, $\delta^{13}C$ is very close to that of the surrounding water (i.e., the isotopic signature of $C_{carb}$ is similar to that of $C_{tot}$) (reviewed in Mackensen & Schmiedl, 2019, Schmittner et al., 2013).

Because different water masses have different origins, they also have different signatures of $\delta^{13}C$ (e.g. NADW is enriched in $\delta^{13}C$, while AABW is depleted in $\delta^{13}C$). Thus, the distribution of $\delta^{13}C$ in the ocean is influenced by ocean overturning circulation and mixing of water masses. The global ocean minimum in $\delta^{13}C$ is found at ~2000 meters depth in the North Pacific. Here, waters that have not been in contact with the atmosphere for a long time, and so have had time to accumulate a lot of depleted $C_{sof}$ along their way through the ocean interior, are carried upward to mid–depths, where local remineralisation further contributes to lowering $\delta^{13}C$.

As a consequence of changes in the ocean processes that control $\delta^{13}C$, the LGM ocean distribution of $\delta^{13}C$ was different from today (Curry & Oppo, 2005, Matsumoto et al., 2002). Proxy records from the LGM indicate that the distribution of NADW was shallower than today (Curry & Oppo, 2005, see Figure 4.5, c.f. NADW and GNADW in Figure 2.1), the Atlantic vertical $\delta^{13}C$ gradient was larger (Curry & Oppo, 2005, and Paper III), and the North Pacific minimum in $\delta^{13}C$ was found at greater depths (Matsumoto et al., 2002, and Paper III). The benthic $\delta^{13}C$ record synthesis of Peterson et al. (2014) is used in in Paper II to examine how well our glacial–like eGENIE model simulations (see Section 3, and 4.4.1) reproduce the spatial pattern of the benthic $\delta^{13}C$ records. This analysis indicates how well these simulations reproduce the glacial ocean circulation and carbon storage. We also make a similar, but more extensive, model–data comparison in Paper III (Section 4.5.1).

Similarly to photosynthetic ocean organisms, land plants are strongly depleted in $\delta^{13}C$ (~-28‰ and -14‰ for the C$_3$ and C$_4$ photosynthetic pathways, respectively) compared to the surrounding atmosphere (~6 to -7‰) (Friedli et al., 1986). If climate changes reduce the terrestrial biosphere, as has been theorised for glacial periods (Shackleton, 1977), the carbon released then enters the ocean carrying with it the
depleted signal of land plants which decreases the global mean $\delta^{13}C$ of the ocean. Several previous studies (e.g., Ciais et al., 2012, Curry et al., 1988, Duplessy et al., 1988, Peterson et al., 2014, Shackleton, 1977, Tagliabue et al., 2009) have used $\delta^{13}C$ proxy records to estimate this whole–ocean change.

**Figure 4.5:** Atlantic sections of $\delta^{13}C$ for the modern day (left panel) and the LGM (18–21 ka, right panel) as drawn by Curry & Oppo (2005), based on their compilation of benthic foraminiferal records for the LGM and previously published work by Kroopnick (1985) for the modern day. $\delta^{13}C$ is reported in $\%$ with respect to the Pee Dee Belemnite (PDB) reference sample.

### 4.5.1 Paper III

In **Paper III**, we take a novel approach to whole–ocean $\delta^{13}C$ by using cGENIE ensemble simulations to extrapolate and interpolate the LGM (19–23 ka) and late Holocene (HOL, 0–6 ka) benthic $\delta^{13}C$ records (Peterson et al., 2014) into regions that are largely unsampled. From the ensemble of simulations, we can then estimate the change in whole–ocean average $\delta^{13}C$ between the LGM and HOL time slices in a way that takes ocean circulation into account. We apply appropriate climatic boundary conditions (sea–level, atmospheric CO$_2$ and $\delta^{13}C$, dust flux, etc.) for each time slice. We then vary selected model parameters (described below) over a wide range of values, and identify the best model representation of the $\delta^{13}C$ records of each time slice within the model ensemble.

Previous model studies of $\delta^{13}C$ have emphasised the importance of denser brines (salt–rich water expelled during ice–formation) that sink to the bottom in the Southern Ocean, and lead to deep ocean stratification, because such scenarios accurately represent glacial $\delta^{13}C$ (Bouttes et al., 2010, 2011). Based on their results, we select to vary the strength of this mechanism in our model ensemble. In line with numerous studies seeking to reproduce glacial and deglacial ocean circulation (e.g., Bouttes et al., 2012, Kageyama et al., 2013, Liu et al., 2009, Menviel et al., 2011, Tagliabue et al., 2009, and references therein), we also apply a freshwater anomaly to the North Atlantic. Building on the results of **Paper I**, and Bouttes et al. (2011), we also assess changes in wind stress scaling and diapycnal diffusivity.
Figure 4.6: Atlantic zonal mean $\delta^{13}C$ for HOL (left panel) and LGM (right panel) from the best–fit cGENIE simulations achieved in Paper III, overlain with the benthic records of Peterson et al. (2014) for the corresponding time slice.

The optimal fits for both time slices are found for the same values of the scaling parameters for wind stress, diapycnal diffusivity and the brine mechanism. However, the best representation of LGM $\delta^{13}C$ is found for a smaller North Atlantic freshwater anomaly compared to HOL. Figure 4.6 exemplifies the model’s ability of reproducing the proxy records in the Atlantic Ocean by showing the best–fit simulations overlain with the proxy $\delta^{13}C$. The model captures both the change in magnitude and in gradient of the $\delta^{13}C$ records between HOL and LGM. The gradient in HOL is small, and the Atlantic is enriched in $\delta^{13}C$ (Figure 4.6, left panel). In the LGM, a water mass with depleted $\delta^{13}C$ values expands into the deep South Atlantic from the Southern Ocean, while the upper North Atlantic is strongly enriched in $\delta^{13}C$ (Figure 4.6, right panel). Based on all ensemble simulations that show high–enough model skill in representing the $\delta^{13}C$ records, we then estimate that the whole–ocean $\delta^{13}C$ was reduced by 0.28 ±0.06‰ in the LGM compared to the late Holocene. For comparison with
previous studies, we convert our estimate of deglacial change in whole-ocean $\delta^{13}C$ into a simple estimate of the corresponding change in terrestrial carbon storage. This simple conversion suggests that an additional $430 \pm 90$ Pg C with a terrestrial $\delta^{13}C$ signature was stored in the ocean water mass during the LGM compared to the late Holocene. Based on the fact that we exclude effects of for example carbon exchange with ocean sediments and changes in terrestrial weathering rates, this is likely an underestimation of the total change in terrestrial carbon storage (Jeltsch-Thömmes et al., 2019).
5. Ocean carbon transport (Paper IV)

How are meridional ocean carbon transports connected globally, and how do different water masses and ocean processes contribute to these transports? In Paper IV, we present a new method for answering these questions, and we apply this method to simulations of the modern-day ocean from NEMO-MEDUSA (see Section 3). The method builds on Groeskamp et al. (2016), who developed a new method for calculating the transport of anthropogenic carbon to the ocean interior based on streamfunctions.

![Global ocean overturning streamfunction from NEMO-MEDUSA simulations](image)

**Figure 5.1**: Global ocean overturning streamfunction from NEMO-MEDUSA simulations (see Paper IV, Methods). The bottom axis shows latitude (°N) and the left axis shows water depth (m). Blue colours indicate clockwise circulation, and red colours anti-clockwise circulation. The overturning is shown in units of Sverdrups [1 Sv = 1 · 10^6 m^3/s], and the ±5 Sv contour is marked by a bold line.

The volume flux of the ocean overturning circulation is often quantified using streamfunctions in depth–latitude space (Figure 5.1), and carbon concentrations are similarly shown as depth–latitude sections through the ocean basins (Figure 5.2). In this paper, we instead use streamfunctions in carbon–latitude coordinates. If $\xi$ is the concentration of some tracer, the streamfunction $\psi(\phi, \xi)$ is defined as the total...
northward volume transport at latitude $\phi$ of water with the tracer concentration less than $\xi$. Integrating $\psi$ over all values of $\xi$ we obtain the total northward tracer transport at this latitude.

When computing $\psi(C_{tot}, \xi)$ for all points on our NEMO–MEDUSA model grid, we get an image of how much water flows through the ocean carrying a specific amount of DIC, and can compute the total meridional carbon transport (see Paper IV, Figure 3). The method allows us to study the Atlantic and Indo–Pacific ocean basins separately, and as different water masses have different signature carbon concentrations, we can identify transports associated with different water masses in each basin. By applying the carbon separation framework, we are also able to analyse the contribution from different carbon species to total ocean carbon transport, globally as well as in different water masses.

As an example of the results obtained by using this method together with the carbon separation framework (Section 4.3), we here show some results for the $C_{sat}$ component, which is the dominant component of $C_{tot}$ (Figure 5.2). The streamfunction (Figure 5.3) shows that high $C_{sat}$ concentrations are set at high latitudes, where deep water is formed. For the Atlantic, we know from Figure 2.1 (top panel) that in the modern day, North Atlantic Deepwater (NADW) is formed in the North Atlantic high latitudes, and should thus correspond to the southward branch of the blue cell 1 in Figure 5.3 (left panel). Meanwhile, Antarctic Bottom Water (AABW) should correspond to the northward branch of the red cell 2. From the red cell 2, it is apparent that when the AABW sinks and moves northward through the deep ocean, it maintains its $C_{sat}$ concentration (cell 2.1), which is expected as $C_{sat}$ can only be altered through air–sea
gas exchange and mixing between water masses. As NADW is less cold than AABW, its maximum concentration of $C_{sat}$ is a bit lower. When AABW turns to flow south, it mixes with NADW. Thus the southward flowing branches of both cells 1 and 2 have the same concentration of $C_{sat}$. In the North Pacific, there is no deep water formation, and the transport of high $C_{sat}$ concentrations is attributed to AABW (extension of cell 2 into cell 2.2, Figure 5.3, right panel). By searching in depth–latitude space (Figure 5.4, panels a and b), for the combinations of latitude and $C_{sat}$ concentrations associated with each of the numbered cells of Figure 5.3, we can identify the cells in geographical space. This confirms our attribution of the blue cell 1 to NADW and the red cell 2.1 to AABW in the Atlantic Ocean, and 2.2 to AABW in the Pacific Ocean.

![Figure 5.3: The $C_{sat}$–latitude streamfunction per basin. The left hand panel shows the Atlantic basin (which includes the Arctic Ocean) and right hand panel shows the Indo-Pacific Ocean. The gray dashed line represents the cape Agulhas latitude. The $C_{sat}$ axes has been reversed so that the tracer acts as a pseudo–depth, where the low values are found near the surface and the higher values at deeper depths. The red (blue) cells represent anti–clockwise (clockwise) circulations. (Figure 4 of Paper IV)](image)

For the global meridional transport of $C_{sat}$, the Indo–Pacific plays a dominant role (Figure 5.4, panel c) with a maximum equatorward transport of 1.1 Pg C per year. In the South Indo–Pacific, most of this transport happens in the upper ocean in the sub–tropical gyre (Figure 5.4, green cell 5 in panels b and e), but $C_{sat}$ is also transported by the interior ocean (Figure 5.4, orange cell 2.2 in panels b and e). However, in the Northern Indo–Pacific, we notice that the deep ocean imprint of $C_{sat}$ circulation is very weak (Figure 5.4, panel b), and the transport of $C_{sat}$ is strongly dominated by surface transport (Figure 5.4, blue cell 3 in panels b and e). In Paper IV, we are able to identify that while $C_{sat}$ is present as a background concentration, the carbon transport in this part of the ocean is mainly attributable to the biological pump.

As the method allows us to estimate carbon transport across latitudes, we can
also make carbon budgets for different regions. Ultimately, we show that we can use the streamfunctions to estimate the turnover times in different overturning cells for the different carbon species (i.e. the time it takes for the carbon to complete a full cycle in a cell), and thus their retention time in different parts of the ocean. Overall, the new method appears promising in terms of applicability for research on ocean carbon transport, especially for the understanding of the contributions of the biological and solubility pumps to transport in different water masses. We however identify some caveats associated with output frequency of the model data, and the effects of diffusion, which prevent the perfect closing of the regional carbon budgets.
Figure 5.4: Panels a and b: The identification in geographical space of different cells for the streamfunction in $C_{sat}$—latitude coordinates for a) the Atlantic and b) the Indo–Pacific basins. The contours represent the fraction of volume at a given latitude and depth contained in the selected cell. Darker colours indicate higher fractions. Panel c: The global meridional transport of $C_{sat}$ and the contribution of the different basins. Panels d and e: The contribution to the meridional transport of each of the cells in the streamfunction in $C_{sat}$—latitude coordinates in d) the Atlantic and e) the Indo–Pacific basin. Each of the cells has an assigned colour which is used for both the transport and the re-projection plots. The transports for the cells have been computed using a threshold of 4 Sv, i.e. the sum of the cells do not fully add up to the total transport.
6. Conclusions and outlook

In Paper I, we investigate the response of the modelled ocean carbon storage to changes in physical processes, and to the strength of the overturning circulation. We also attribute the response to the relevant carbon system process. We find a negative linear relationship between ocean carbon storage and the net strength of the global overturning circulation. In addition, based on the already–present amount of biologically–sourced carbon in the model ocean, we evaluate the model response to a perturbation of the biological carbon capture. Here, we find that the initial state predicts the model’s response to the perturbation. From this, we conclude that initial state differences in ocean carbon storage can be important to consider, for example in the interpretation of model–intercomparison studies.

In Paper II, we evaluate if flexibility in the elemental (carbon to phosphorus) composition of photosynthetic organisms in the ocean can be of importance for the model’s ability to reproduce glacial atmospheric CO\(_2\). We do this by comparing two different model versions, with constant or flexible ratios of the two selected elements. We conclude that the flexible ratios, as described by Galbraith & Martiny (2015), allow for 25% additional lowering of the atmospheric CO\(_2\), and brings the atmosphere of our most glacial–like simulation closer to proxy records from the LGM. The results of Paper II demonstrate the importance of biological adaptability to the surrounding conditions for the outcome of glacial simulations. The Galbraith & Martiny (2015) parameterisation is computationally cheap and could be considered as a first step for improvement of the biogeochemical models included in the Paleo Model–Intercomparison Project (PMIP) that currently use constant C/P ratios. Future efforts should also evaluate the effect of flexible C/P in other climate change scenarios. Ideally, observational programs should measure C/P of plankton as a complement to measurements of DIC and P. If spatial coverage of such information increased, it would allow for more systematic testing of the performance of biogeochemical models in this respect.

In Paper III, we use a numerical model to extrapolate and interpolate the existing sparse records of \(\delta^{13}C\) from the benthic layer, just on top of the ocean sediments, for the late Holocene (0–6 ka), and the LGM (19–23 ka) (Peterson et al., 2014). By running a series of simulations, where we vary selected parameters that influence the water mass distribution in the ocean over a pre–defined range, we can isolate the simulations with the best fit to each time period in the proxy records. Based on all ensemble simulations that show high–enough model skill in representing the \(\delta^{13}C\) records, we then estimate that the whole–ocean \(\delta^{13}C\) was reduced by 0.28 ±0.06\% in the LGM compared to the late Holocene. From this, we draw conclusions about the transfer of terrestrial carbon to the ocean water mass carbon reservoir. As demonstrated by Jeltsch-Thömmes et al. (2019), the effects of ocean sediments could be important for
estimates of glacial–interglacial changes in terrestrial carbon storage. This suggests our experiments should be repeated with interactive sediments. For increased confidence in our results, we would also like to compare our ensembles to proxy records of radiocarbon.

Papers I–III are all based on simulations with cGENIE, which is a model of intermediate complexity. The low spatial and temporal resolution of the model, in combination with the simplified physics, puts constraints on the realism of the simulations. Thus, it would be beneficial to repeat these studies with higher–resolution models, in order to test the validity of the results. However, state–of–the–art GCMs with ocean biogeochemical modules, such as NEMO–MEDUSA, are generally too computationally expensive to run to equilibrium for the carbon cycle. Therefore, initial efforts to repeat similar experiments should aim to use a model with improved ocean resolution, and an interactive atmosphere for additional climate feedbacks. In addition, the contemporary biogeochemical models used with GCMs do not include the pre–formed tracers used in Papers I and II. These papers demonstrate, however, the usefulness of such tracers, and future efforts to improve biogeochemical models should consider the possibility to simulate pre–formed tracers.

In Paper IV, a new method for meridional ocean carbon transport, based on streamfunctions in carbon–latitude space, is introduced. We apply the method to model simulations of modern–day climate, and isolate contributions from physical– and biological processes in the ocean carbon system. The results highlight some interesting features of the carbon transport and storage in the modern ocean, and illustrates the role of different water masses in the global meridional redistribution of carbon. This method could be used to elucidate changes in meridional ocean carbon transport across climate states, if applied to simulations of different time periods run with the same model.

ARGO (2019). http://www.argo.net. 11


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Stockholm

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