



Dissolution of CaCO₃ in the present and glacial ocean: A comparison of the effects of different dissolution

parameterizations

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MASTERS THESIS

SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF

MASTER OF SCIENCE IN ENVIRONMENTAL PHYSICS

Supervised by

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November 3, 2017



Declaration

Here, I want to declare that this thesis work is done by myself and also the writing is based on my research findings.

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Signature

Abstract

The production of the calcium carbonate minerals calcite and aragonite in the ocean is primarily done by different pelagic calcifying organisms: coccolithophorids, foraminifera and pteropods. The contribution of corals to the production of $CaCO_3$ is comparatively small. The surface ocean is supersaturated with respect to the two minerals forms of CaCO₃: aragonite and calcite, while the deep ocean is undersaturated. Most of these calcium carbonate minerals produced near the surface ocean sink through the water column and mainly dissolve in the deep ocean below the saturation horizon where the solubility product of the minerals increases due to increased pressure. CaCO₃ formation in the surface ocean and dissolution in the deeper ocean both affect dissolved inorganic carbon and total alkalinity and also the oceanic pCO_2 . In this study, a global biogeochemical model (REcoM) is used to analyze the production and dissolution of CaCO₃ for the Last Glacial Maximum (LGM) and present day with two different set up of dissolution rate: one is that the dissolution rate of CaCO₃ is assumed constant when it sinks through the water column (λ does not depend on the degree of saturation (Ω)), in the other λ has been made depend on Ω . In REcoM, biogenic CaCO₃ production is restricted to phytoplankton. In comparison with present-day observations, a model simulation with uniform dissolution already does a good job at reproducing the global patterns of DIC, alkalinity and Ω although some regional differences remain: too high DIC concentrations in between 800 m to 1200 m ocean depth, somewhat too high alkalinity concentration in the depth between 1200 m to 2000 m and higher Ω than observed in the Atlantic Ocean and the Indian Ocean. In one part of this study, it is tested whether changes in the parameterization of the CaCO₃ dissolution rate in the model can improve the distribution. Making the dissolution depend on Ω leads to improve the global oceanic distribution of DIC, alkalinity and Ω in some respect. One thing that does not change is the intermediate maximum in DIC that comes from the too much remineralization of organic matter. The LGM simulation reproduces a colder, more salty and more alkaline ocean. Changes in biological production lead to a redistribution of DIC and alkalinity between the deep Atlantic and Pacific Ocean. The larger volume of AABW in the Atlantic Ocean leads to a further increase of DIC and alkalinity there. An overall higher LGM surface ocean calcite saturation state is driven by lower LGM pCO2 that decreases LGM surface DIC concentration. The LGM Atlantic and Pacific deep ocean calcite saturation state evolved in different direction affected by the biological production and carbon export to deep ocean. Effect of iron fertilization that would lead to changes in POC export is neglected in the LGM model run.

Acknowledgment

Firstly, I would like to express my sincere gratitude to my thesis supervisor Dr. Christoph Völker for his continuous support, motivation, patience, and immense knowledge. His guidance and teaching helped me in all the time of my thesis and writing. I would also like to thank Dr. Völker for all his programming tips and for helping me to learn the usage of various programming languages and tools. I could not imagine having a better mentor and supervisor for my master thesis. I would also like to acknowledge Prof. Dr. Gerrit Lohmann, as the second reader of this thesis, and I am gratefully indebted to him for his very valuable comments during thesis work. I would also like to thank Dr. Judith Hauck for helping me to understand the model sometime and also for discussion about science. My sincere thanks also goes to Dr. Xu Zhang for his support to understand the LGM part of my thesis. Special thanks to my colleagues at the Alfred Wegener Institute and every member of the PEP programme at the University of Bremen for their contributions towards the completion of this programme. I would like to thank Razib Vhuiyan, Anna Pagnone and Essowe Panassa for their friendly motivation throughout the thesis period. Last but not the least, I would like to express my very profound gratitude to my parents and family members for providing me continuous encouragement and unfailing support throughout my study. This accomplishment would not have been possible without them.

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Abbreviations

AABW	Antarctic Bottom Water
AMOC	Atlantic Meridional Overturning Circulation
CCD	Calcite Compensation Depth
CORE	Common Ocean-Ice Reference Experiment
DIC	Dissolved Inorganic Carbon
DIN	Dissolved Inorganic Nitrogen
DOC	Dissolved Organic Carbon
DOE	Department Of Environment
DON	Dissolved Organic Nitrogen
GNAIW	Glacial North Atlantic Intermediate Water
GLODAP	Global Ocean Data Analysis Project
LGM	Last Glacial Maximum
MITgcm	Massachusetts Institute of Technology general circulation model
NADW	North Atlantic Deep Water
NPIW	North Pacific Intermediate Water
PIC	Particulate Inorganic Carbon
PISCES	Pelagic Interactions Scheme for Carbon and Ecosystem Studies
POC	Particulate Organic Carbon
REcoM	Regulated Ecosystem Model
SST	Sea Surface Temperature
TA	Total Alkalinity
WOA09	World Ocean Atlas 2009

1 Introduction

1.1 Production of CaCO₃

The oceanic precipitation of CaCO₃ in the open ocean is primarily done biologically by one phytoplanktonic group: coccolithophorids, and two zooplanktonic groups: foraminifera and pteropods. They predominantly occur near the ocean surface but foraminifera also occur at the bottom of the ocean [Sarmiento and Gruber, 2006]. CaCO₃ is precipitated usually in the form of calcite and aragonite, two common crystal forms of CaCO₃. Coccolithophorids and most foraminifera produce calcite whereas aragonite is produced by pteropods and also by some foraminifera [Zeebe and Wolf-Gladrow, 2001]. Among them, coccolithophores are considered to be the most productive calcifying group [Westbroek et al., 1993] over a large area of the world ocean because of their formation of intensive blooms, especially in subpolar regions [Brown and Yoder, 1994]. Corals are also one of the major calcifying groups in the world ocean and produce a significant amount of calcium carbonate in near-shore environments. About 0.3 Pg C yr⁻¹ of CaCO₃ is produced by coral reefs mostly in the form of high-magnesium calcite or aragonite, which is roughly a third of the open ocean CaCO₃ production [Milliman and Droxler, 1996]. Some part of this CaCO₃ could get transported and dissolved into the open ocean. Milliman et al. [1999] state that this transport can be up to 0.1 Pg C yr⁻¹.

By the following calcification equation, it can be seen that the formation of $CaCO_3$ from calcium and bicarbonate ion produces aqueous CO_2 which can be used in photosynthesis as source of inorganic carbon [Zondervan et al., 2001]

$$2HCO_3^- + Ca^{2+} = CO_2 + CaCO_3 + H_2O$$
(1)

Calcification affects the global and regional carbon budgets by the production of CO_2 and $CaCO_3$ and also by fixing of HCO_3^- [Balch et al., 2007]. Recent global estimation of carbonate production is 1.3×10^{14} moles $CaCO_3$ yr⁻¹ equivalent to 1.6 Gt Particulate Inorganic Carbon (PIC) yr⁻¹ [Balch et al., 2007]. Berelson et al. [2007] estimates the global average carbonate production ranging from 0.5 to 1.6 Gt PIC yr⁻¹ whereas the estimated carbonate export (vertical flux of carbonate out of the productive upper layer of the ocean) ranges between 0.4 to 1.8 Gt PIC yr⁻¹ based on the analysis of carbonate rain ratio (global average export ratios of CaCO₃ to organic carbon) in the water column and on sediment dissolution rates. The difference between production and export can be compared with the oceanic organic carbon cycle. Recently [Jin et al., 2007] summarized global estimates of organic matter varies in the range of 40 to 50 Gt POC

yr⁻¹. The ratio of PIC to particulate organic carbon (POC) is estimated about 0.06 ± 0.03 based on the analysis vertical gradients of potential alkalinity and nitrate [Sarmiento et al., 2002]. Recently Balch et al. [2005] estimate that the ratio between CaCO₃ and POC in the euphotic zone is about 0.05 ± 0.01 .

1.2 Dissolution of CaCO₃

A large fraction of the produced CaCO₃ remains intact when the planktonic organisms producing it die or get eaten and subsequently sinks. CaCO₃ that is leaving the ocean surface can either be dissolved throughout the water column or at the ocean floor, or get buried [Battaglia et al., 2016]. Dissolution of calcium carbonate is mainly dependent on the saturation state of seawater (Ω) with respect to calcite or aragonite [Sarmiento and Gruber, 2006]. The seawater saturation (Ω) with respect to calcite or aragonite (equation 15) given in chapter 2.1 and can be defined by the product of $[CO_3^{2-}]$ and $[Ca^{2+}]$ ion concentrations divided by the stoichiometric solubility product at the in situ temperature, pressure and salinity [Chung et al., 2003]. The dissolution of CaCO₃ minerals is thermodynamically possible when the calcium and carbonate ion concentrations product is below the saturation product in the surrounding environment. Values of omega larger than one ($\Omega > 1$) represent undersaturated condition of seawater while values of omega smaller than one ($\Omega < 1$) represent undersaturation [Zeebe and Wolf-Gladrow, 2001].

The saturation product of all minerals strongly increases with increasing pressure [Mucci, 1983]. The increase in the pressure with depth leads to increases in solubility of carbonate minerals, causing a decrease of Ω with depth in the ocean. In addition the respiration of organic matter decreases the carbonate ion concentration in the deeper ocean leading to a further decrease in Ω . With respect to the mineral phases of calcium carbonate most of the upper parts of the ocean water column are supersaturated and deep ocean waters are undersaturated [Jansen et al., 2002].

The depth that separates the supersaturated and undersaturated layer is called saturation horizon. This depth is significantly deeper for calcite than aragonite, as aragonite is more soluble than calcite, and also varies from ocean to ocean, being low in high latitudes and the Indian Ocean, high in the Pacific due to the increase of remineralization products with water mass age [Pachauri and Reisinger, 2007].

Figure (1) below shows the difference in saturation horizon of calcite and aragonite in the North Atlantic and North Pacific Ocean. The saturation state of calcite and aragonite is much lower in the North Pacific than in the North Atlantic Ocean. The old ocean waters in the deeper Pacific contain more DIC than in the fresh as Atlantic ocean, due to organic matter remineralization in the deep water. Increased DIC results in a lowering of the carbonate ion concentration in the Pacific Ocean that makes the ocean water more corrosive. This phenomenon is responsible for the difference in lysocline depth both for calcite and aragonite in the North Pacific and North Atlantic Ocean. The lysocline depth is the place in the water column where undersaturation with respect to calcite or aragonite results in a rapid increase in the CaCO₃ dissolution rate [Morse, 1974]. With respect to calcite, lysocline depth is about 4000 m (for aragonite, less than 500m) in the Pacific Ocean and about above 4500m (for aragonite, 3000 m) in the Atlantic Ocean [Zeebe and Wolf-Gladrow, 2001].



Figure 1: Schematic diagram of the saturation state of ocean water with respect to calcite and aragonite in the Atlantic and Pacific Ocean as a function of depth. Supersaturation and undersaturation are separated by the vertical dashed line [Zeebe and Wolf-Gladrow, 2001].

1.2.1 Water column dissolution

This section deals with the water column dissolution of biogenic calcium carbonate minerals while they are sinking through the water column. In general, the dissolution kinetics of calcium carbonate are described by a higher order dependency on the degree of CaCO₃ saturation [Gehlen et al., 2007]. For undersaturated water ($\Omega > 1$), one can write the CaCO₃ dissolution rate reaction by following [Morse and Berner, 1972].

$$\frac{d[\text{CaCO}_3]}{dt} = -[\text{CaCO}_3] \cdot k_{\text{CaCO}_3} (1 - \Omega)^n$$
(2)

where k_{CaCO_3} and [CaCO₃] are the dissolution rate and concentration of CaCO₃ respectively, and n is the kinetic order of reaction.

In the case of calcite minerals, Keir [1980] proposed a reaction rate order of 4.5 on the basis of laboratory dissolution studies. However, Hales and Emerson [1997a] reevaluated the [Keir, 1980] data and argued that the dissolution rate is linearly dependent on undersaturation (n = 1). Furthermore, first order calcite dissolution kinetics give a better consistency with the interpretation of *p*H measurements in-situ pore water [Hales and Emerson, 1997a,b]. Recently Arvidson et al. [2003] give an extended reevaluation of carbonate dissolution kinetics and proposed that the reaction is nonlinear, that in most cases the value of n is larger than 1.

The time that sinking particles spend in the water column before arriving at the ocean floor is very short in comparison to the timescale of calcite dissolution in the undersaturated water. That is why it is assumed that the dissolution of carbonate minerals mostly occurs in the sediments [Jansen et al., 2002].

Milliman et al. [1999] calculated however that about 60 - 80 % of the total calcium carbonate dissolution takes place in between 500 and 1000 m depth in the upper ocean, although ocean waters are mostly supersaturated in this depth range with respect to both aragonite and calcite. A possible explanation is that many CaCO₃ particles do not sink alone, but together with other particles that contain organic carbon. The respiration of this organic matter can then create a chemical acidic micro-environment around the aggregate, enabling the dissolution in oceanic upper layer supersaturated waters [Jansen et al., 2002].

Jansen et al. [2002] also suggest that water column carbonate dissolution is possible when considering only the calcite, because the sinking rate of individual coccoliths and coccolithophorids is slow, so that it can make possible water column dissolution. The sinking rate of foraminifera and pteropods is so fast that almost no dissolution occurs before reaching the seafloor.

1.2.2 CaCO₃ dissolution in the sediment

Sediment dissolution processes causing fluxes of Ca^{2+} and alkalinity from sediment play a much more crucial role than water column dissolution for the $CaCO_3$ budget in the world ocean [Sarmiento and Gruber, 2006] because the dissolution of $CaCO_3$ mainly occurs in deep ocean undersaturated water. The calcite compensation depth (CCD) is the depth in which the dissolution rate of calcite minerals in sediments is balanced by the supply of the calcite minerals. At this depth, sediments have lost their all calcite minerals due to dissolution [Zeebe and Wolf-Gladrow, 2001]. The CCD strongly varies throughout the world ocean. CCD gets shallower as

Atlantic deep water moves to the Pacific Ocean through the Indian Ocean. The lysocline is generally consistent with the saturation horizon depth and this consistency imply that the variation of the thermodynamic driving factor plays a major role in $CaCO_3$ preservation [Sarmiento and Gruber, 2006].

In the sediment, the dissolution of $CaCO_3$ can also be caused by the process of remineralization. Carbonic acid is produced by organic matter remineralization process within the sediments. Dissolution powered by acid produced in the sediment column is sensitive to the rate of acid production and also to its depth distribution [Boudreau and Canfield, 1993]. The ratio of sinking organic matter (POC) to CaCO₃ (PIC) in the deep ocean is on the order of 1:1, [Emerson and Bender, 1981, Archer, 1991] so adequate CO₂ will be available for the dissolution of all CaCO₃ in the sediment if all organic carbon material is going through the remineralization process [Sarmiento and Gruber, 2006].

But the permanent burial of a significant portion of the deposited calcium carbonate indicates the variation in relation between organic matter remineralization and CaCO₃ dissolution. The reason behind this decoupling is that the remineralization of organic matter occurs very fast in the upper sediment layer while the dissolution kinetics of CaCO₃ seems to be slower [Sarmiento and Gruber, 2006]. This difference creates a vertical separation between the very near surface and the deeper layers in the sediments. In consequence, a considerable amount of the free protons from the remineralization in the sediment near surface diffuses out of the sediments and is buffered by the lowermost bottom waters, decreasing the efficiency rate of respiratory-driven dissolution of CaCO₃ [Hales, 2003].

1.3 Effects of CaCO₃ formation and dissolution on oceanic and atmospheric carbon

 CO_2 gas exchange between atmosphere and ocean is regulated by the two marine carbon pumps which are driven by the production of organic matter and calcium carbonate respectively and subsequent sinking to the depth. CO_2 gas exchange depends on the difference between the pCO_2 in atmosphere and ocean. The oceanic pCO_2 in turn depends on DIC and alkalinity. The organic and $CaCO_3$ pump transport organically bound carbon and $CaCO_3$ from the production site near the surface into the deep ocean, where they slowly get remineralized and dissolved. Both pumps change the DIC and alkalinity at the ocean surface, which affects the pCO_2 [Jansen, 2001].

From figure (2) it can be seen that the pCO_2 increases with increases of DIC and also with



Figure 2: Formation and dissolution effect of $CaCO_3$ on total alkalinity and dissolved inorganic carbon as well as on oceanic pCO_2 from [Sigman and Boyle, 2000].

decreases of alkalinity. The resulting effects of an imbalance between $CaCO_3$ production and loss on DIC and alkalinity are shown by the dashed arrows. Oceanic alkalinity and DIC decreases in a 2:1 ratio through the production of $CaCO_3$. A higher input of dissolved calcium carbonate than the burial therefore lowers the pCO_2 of surface waters and increases the oceanic uptake of CO_2 from the atmosphere [Zeebe and Wolf-Gladrow, 2001].

The solid arrows show the effect of the export production (rain of biogenic materials to the deep ocean from the surface). DIC is removed from the surface ocean by export production whereas alkalinity increases in a modest way because of the associated uptake of phytoplanktonic nitrate [Sigman and Boyle, 2000]. Deep ocean DIC and alkalinity are also affected by the export production resulting in a lowering of deep water carbonate ion concentration. This is because, produced surface ocean organic carbon releases DIC by the bacterial microbial oxidation processes in the ocean interior and lowers the deep water carbonate ion concentration [Jansen, 2001]. This processes again affects the burial rate of calcium carbonate in the ocean sediments, which further alters the surface waters pCO_2 through its impact on the total ocean CaCO₃ balance (dashed arrows).

2 Model and methods

In this study, a physical and a biogeochemical model is used to simulate the effect of production and dissolution of $CaCO_3$ on the global carbon cycle. As a physical model, the Massachusetts Institute of Technology general circulation model (MITgcm) [Marshall et al., 1997] and as biogeochemical model, the Regulated Ecosystem Model version 2 (REcoM-2) is used. Both the physical and biogeochemical model are described here only in their most important aspects with respect to the carbon cycle. To investigate the glacial-interglacial changes of $CaCO_3$ dissolution, four model simulations have been performed. A summary of these four simulations with their experiment characteristics is shown in table 1.

Name	Boundary	Ω dependency of CaCO ₃ dissolution	Length of model
	conditions		integration (years)
EXP 01	present-day	Uniform dissolution	1000
EXP 02	present-day	Dissolution depends on Ω	1000
EXP 03	21 ka	Uniform dissolution	3000
EXP 04	21 ka	Dissolution depends on Ω	3000

Table 1: Experimental design of the four different model simulations in this study.

Chapter 3 discusses the baseline experiment EXP 01 and compares the results to a climatology of observations (GLODAP.v2). Results from LGM simulation with uniform dissolution (EXP 03) are discussed in chapter 4 and compared to the EXP 01. Chapter 5 discusses the experiments EXP 02 in which dissolution has been made to depend on Ω and compares it to the baseline experiments EXP 01 for present day. The results from LGM model run with the Ω dependent dissolution (EXP 04) have been not analyzed further in this study because the run produced unrealistic DIC values and could not be repeated in time. Unrealistic values of DIC were caused by the problems from the convergence of the calculation of *p*CO2 from DIC and alkalinity.

2.1 Calculations of the carbonate system in seawater

To analyze both model and observational data, a few calculations of the seawater carbonate chemistry have to be performed. Here therefore I start with a description of these calculations.

Aqueous carbon dioxide (CO₂), bicarbonate HCO_3^- and carbonate ion CO_3^{2-} are the main three forms of carbon dioxide in the Ocean [Zeebe and Wolf-Gladrow, 2001]. The atmosphere -

ocean exchange of CO_2 depends on the balance between dissolved CO_2 and atmospheric pCO_2 [figure (3)]. Dissolved CO_2 from atmosphere reacts with seawater. The chemical equilibrium



Figure 3: Schematic diagram of the carbonate system in seawater [p.3 Zeebe and Wolf-Gladrow, 2001, chapter 1].

of the carbonate system can be described by the following equation:

$$CO_2 + H_2O \stackrel{K_1}{\rightleftharpoons} HCO_3^- + H^+ \stackrel{K_2}{\rightleftharpoons} CO_3^{2-} + 2H^+$$
(3)

K₁ and K₂ are the first and second equilibrium constant of the carbonate system respectively.

Dissolved inorganic carbon (DIC) is defined by sum of the concentrations of the dissolved forms of CO_2 , HCO_3 , and CO_3^{2-} . In the following, brackets denote the concentration.

$$DIC = [CO_2] + [HCO_3^-] + [CO_3^{2-}]$$
(4)

Besides DIC, Alkalinity is another important quantity for the carbonate system that is mainly related to the charge balance in seawater [Zeebe and Wolf-Gladrow, 2001]. Total alkalinity (TA) can be outlined as:

$$TA = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] - [H^+] + \text{minor species}$$
(5)

The minor species further contain small contributions from nutrients that are neglected in this calculation. Carbonate alkalinity (CA) is a part of total alkalinity (TA) and is defined by the following equation:

$$CA = [HCO_3^-] + 2[CO_3^{2-}]$$
 (6)

In the ocean, the dissolution of calcium carbonate is considered to mainly depend on the saturation state of either calcite or aragonite, the two main crystal forms of $CaCO_3$. The saturation

state is primarily determined by the carbonate ion concentration [Zeebe and Wolf-Gladrow, 2001]. The final goal of these calculations is to calculate the saturation state of calcium carbonate in the form of calcite to understand the dissolution of $CaCO_3$ in the world ocean from observational and model data. To do that one has to go through several steps: The first step would be to calculate the equilibrium stability constants K_1 , K_2 for carbonic acid dissociation, and K_b and K_w for boric acid and for water respectively. The equilibrium constants are defined by the following equations:

$$K_1 = \frac{[\text{HCO}_3^-][\text{H}^+]}{[\text{CO}_2]}$$
(7)

$$K_2 = \frac{[\mathrm{CO}_3^{2-}][\mathrm{H}^+]}{[\mathrm{HCO}_3^{1-}]}$$
(8)

$$K_b = \frac{[B(OH)_4^-][H^+]}{[B(OH)_3]}$$
(9)

$$K_w = [\mathrm{H}^+][\mathrm{OH}^-]$$
 (10)

The constants are given as empirical functions of temperature and salinity. For the equations of equilibrium constants, [Zeebe and Wolf-Gladrow, 2001] have been followed who in turn cite [DOE, 1994].

To calculate the carbonate system, also need to care about Boric acid $B(OH)_3$ and borate $B(OH)_4^-$ because of their contribution to total alkalinity (TA) [Zeebe and Wolf-Gladrow, 2001]. The total boron concentration B_T

$$B_T = [B(OH)_4^-] + [B(OH)_3]$$
(11)

mainly depends on seawater salinity and the relation is also given in [Zeebe and Wolf-Gladrow, 2001]. The equilibrium between boric acid and borate is given by

$$B(OH)_3 + H_2O \stackrel{K_b}{\rightleftharpoons} B(OH)_4^- + H^+$$
(12)

where K_b is the equilibrium constant for boric acid dissociation defined by equation (9)

Pressure has also a small effect on equilibrium constants. Millero [1995] has given a correction for the dependency of the equilibrium constants on pressure. The equation by which one can calculate the effect of pressure on equilibrium constants is also given in [Zeebe and Wolf-Gladrow, 2001]. With the calculated stability constants and DIC, TA specified and B_T , one can calculate the *p*H. *p*H is the negative decadal logarithm of H⁺ ion concentration. *p*H can be calculated from DIC and TA by inserting the equilibrium relations from equation (7) and equation (9) into the equation for DIC and TA (equation (4) and equation (5) respectively). This results in two equations for the two unknowns [CO₂] and [H⁺], which can be combined to one

fifth order polynomial for $[H^+]$ alone. Solving this polynomial will give H^+ ion concentration. With $[H^+]$ given, one can calculate the carbonate ion concentration as a function of DIC.

$$[CO_3^{2-}] = \frac{[DIC]K_1K_2}{[H^+]^2 + [H^+]K_2 + K_1K_2}$$
(13)

Finally, the solubility product of calcite needs to be calculated. The solubility product K_{sp} defines the concentration of $[CO_3^{2-}]$ and $[Ca^{2+}]$ in thermodynamic equilibrium with solid calcite and can be outlined by the following equation [Zeebe and Wolf-Gladrow, 2001].

$$K_{sp} = [\operatorname{Ca}_{eq}^{2+}] \cdot [\operatorname{CO}_{3eq}^{2-}]$$
(14)

Oceanic $[Ca^{2+}]$ variations are quite small and closely related to (proportional) variations in salinity. The relation between salinity and $[Ca^{2+}]$ has been taken from [Zeebe and Wolf-Gladrow, 2001]. So now at the end, one can calculate the saturation state of calcium carbonate (Ω) , that is the function of carbonate ion concentration. The CaCO₃ saturation state of seawater Ω can be expressed as:

$$\Omega = \frac{[Ca^{2+}][CO_3^{2-}]}{K_{sp}}$$
(15)

2.2 The physical model

The MITgcm is a numerical model based on the Navier Stokes equation and the conservation of mass, salt and energy, that has been developed for the study of the large-scale ocean, atmosphere and climate. Because of its possibility for non-hydrostatic modelling, it can be used for small scale process as well [Adcroft et al., 2004]. MITgcm determines the advection and mixing of tracers as a result of the circulation and physical state of ocean i.e. of its velocity, temperature, salinity and pressure fields which are used as prognostic variables in this ocean circulation model [Adcroft et al., 2004]. The setup of the MITgcm model that we use is designed globally at coarse resolution on a grid with 2° longitudinal spacing and between 0.38° and 2° latitudinal spacing. The model domain reaches from 80° S to 80° N, excluding the Arctic Ocean [Hauck et al., 2013]. For a better resolution of the Southern Ocean, the latitudinal spacing of this model has been made 2° times the cosine of latitude. For better resolution of the equatorial current system, resolution around the equator has been increased to about half a degree [Aumont et al., 1999]. The model consists of 30 vertical levels, with layer thickness increasing from 10 m at the surface to 500 m below a depth of 3700 m [Hauck et al., 2013]. The model is forced with an annual climatology of daily wind speed, air temperature, humidity and monthly precipitation and river runoff taken from the CORE data set [Large and Yeager, 2004]. From

there forcing fields, heat and freshwater fluxes and wind stress are calculated. For the LGM simulations, monthly averaged atmospheric forcing fields were taken from coupled atmosphereocean simulations performed with COSMOS [Zhang et al., 2013] in which boundary conditions and external forcing were imposed according to the PMIP3 protocol for the LGM.

The present day model integration is done over a thousand years. The model is integrated from a state of rest; initial conditions for temperature, salinity, nitrate and silicate were taken from the World Ocean Atlas 2009 (WOA09) [Locarnini et al., 2010, Antonov et al., 2010, Garcia et al., 2010].

The LGM Model run has been integrated over the time of 3000 years. For the LGM runs, sea level has been lowered by 116 m to account for the storage of water in land ice. Total salinity has been made to be conserved, which leads therefore to an increase in ocean salinity by a constant value of around 1 psu. Temperature has been initialized with present-day values, leaving it to the model to equilibrate temperature with the given glacial atmospheric forcing.

The total inventory of tracers (alkalinity, DIC, silicate and phosphate) has been conserved between the present day and LGM runs, i.e. the average concentration has been increased to compensate for the lower ocean volume during the LGM. The partial pressure of atmospheric carbon dioxide pCO_2^{atm} has been set to a fixed pre-industrial value of 280 ppm to a glacial value of 180 ppm for the LGM [Völker and Köhler, 2013].

The LGM model run uses the same dust deposition fields as for the present day. In that respect the LGM state is not realistic as in the glacial time dust deposition was stronger because atmosphere was dryer and also because of more exposed shelves. This study therefore analyzes the effect of the physical changes (atmospheric temperature, wind speed, sea level etc.) only but not the effects of a changed iron input. One may assume that the additional iron fertilization would lead to increase in LGM POC export in some parts of the Southern Ocean, while the runs shown here show a global decrease of export (chapter 4.3).

2.3 The biogeochemical model

The Regulated Ecosystem Model, version 2 (REcoM-2) is used as biogeochemical model in this study. REcoM is based on the [Geider et al., 1998] model in which the internal stoichiometry of phytoplankton cells varies with environmental conditions like light, temperature and nutrient supply. As a result the biochemical composition i.e. the ratio of carbon to chlorophyll (C: Chl) and the ratio of carbon to nitrogen (C: N) in pytoplankton also change with various growth conditions [Geider et al., 1998].

An overall summary of the REcoM-2 model is illustrated in figure (4). In total the REcoM-2



Figure 4: Schematic diagram of the biogeochemical REcoM-2 model compartments, [Schourup-Kristensen et al., 2014]

model contains 21 tracers and is divided into different compartments. From figure (4) one can see that the model contains two different functional types of phytoplankton, i.e. nanophytoplankton and diatoms which contain carbon, nitrogen and chlorophyll. Only the nanophytoplankton contains CaCO₃ and only the diatoms contain silica. The production of calcium carbonate is described as a function of the gross production of nanophytoplankton [Hauck et al., 2013]. The model also consists of one zooplankton and detritus compartment with organic forms of the main nutrients [Hauck et al., 2013]. The zooplankton compartment consists of a nitrogen and carbon pool. Phytoplankton cells are grazed by zooplankton which produce detritus. The zooplanktonic nitrogen and carbon pool can be increased by phytoplankton grazing and decreased by the process of excretion of dissolved organic carbon (DOC) [Hauck et al., 2013]. The heterotrophic carbon pool is the imbalance between uptake of carbon by grazing and loosing by mortality [Hauck et al., 2013]. Detritus compartment contains organic carbon, nitrogen, biogenic silica, iron and calcium carbonate. The detritus sinking speed increases with depth [Kriest and Oschlies, 2008]. The model also contains another compartment with dissolved organic nitrogen and carbon. The fifth compartment of the REcoM-2 model consists of dissolved substances i.e. the nutrients, dissolved inorganic nitrogen (DIN), Dissolved silicate (DSi) and dissolved iron (DFe), dissolved inorganic carbon (DIC) and total alkalinity (TA) [Schourup-Kristensen et al., 2014]. REcoM-2 model also has sediment compartments for carbon, nitrogen, silica and calcium carbonate, that mainly consist of only the detritus sinking layer. Remineralization occurs in this compartment and by this process nutrients are restored to the water column [Schourup-Kristensen et al., 2014]. In the present model setup, the dissolution rate of CaCO₃ does not depend on saturation state but is described as a temperature dependent first-order dissolution reaction process [Yamanaka and Tajika, 1996].

From the Global Ocean Data Analysis Project (GLODAP) data set [Key et al., 2004] the RecoM-2, model initialization is done for the tracers of dissolved inorganic carbon (DIC) and total alkalinity (TA) [Schourup-Kristensen et al., 2014]. The tracers for DSi and DIN were set with values obtained from the data of Levitus World Ocean Atlas climatology of 2005 [Garcia et al., 2006]. PISCES model output was used as initialization for the iron field [Aumont et al., 2003] since no global observational field is available.

2.3.1 Processes that affect alkalinity and dissolved inorganic carbon in the model

The biological tracers (i.e. concentration of nutrients, biomass etc) are altered by the physics of the ocean through advection and diffusion and by biological processes in biogeochemical models. Every biogeochemical tracer in the model fulfills the mass balance. The rate of change of the concentration for a given biological tracer T can be described by the following equation:

$$\frac{\partial T}{\partial t} = F_T + SMS_T \tag{16}$$

where F_T stands for the physical transport of the tracers by advection and diffusion and SMS_T stands for biological sources minus sinks, corresponding to the changes caused by biological processes.

For DIC and alkalinity, we have the following two equations for the SMS term [Hauck et al., 2013]. The sources for DIC are assumed respiration by diatoms, nanophytoplankton, and heterotrophs. The dissolution of calcium carbonate and remineralization of dissolved organic carbon (DOC) are also sources of DIC in the model [Hauck et al., 2013]. Formation of calcium carbonate and the fixation of carbon by primary producers are the sinks of DIC. Air – sea flux of CO_2 has also impact on surface DIC concentration.

$$SMS_{DIC} = (r_{phy} - p_{phy}) \cdot C_{phy} + (r_{dia} - p_{dia}) \cdot C_{dia} + r_{het} \cdot C_{het} +$$
(17)
$$\rho_{DOC} \cdot f_T \cdot DOC + \lambda \cdot CaCO_{3det} - calcification$$

here C_{phy} , C_{dia} and C_{het} are the carbon biomass of phytoplankton, diatoms and heterotrophs, respectively, r_{phy} , r_{dia} and r_{het} are the respiration rates of phytoplankton, diatoms and heterotrophs, respectively, p_{phy} and p_{dia} are the photosynthesis rates of phytoplankton and diatoms respectively, the remineralization of DOC is represented by ($\rho_{DOC} \cdot f_T \cdot DOC$) and λ is the calcite dissolution rate, which is explained below in more detail.

The alkalinity balance is determined by precipitation and dissolution of calcium carbonate, phytoplanktonic uptake of phosphate and nitrate, and remineralization of dissolved organic matter [Wolf-Gladrow et al., 2007]. Alkalinity is decreased during calcification and increased during the dissolution of $CaCO_3$. Phosphorus is taken into account assuming a constant ratio of N:P of 16:1. Alkalinity is increased by nitrogen assimilation and by the dissolution of calcium carbonate whereas production of $CaCO_3$ and dissolved organic nitrogen (DON) remineralization act as sinks.

$$SMS_{TA} = (1 + 1/16) \cdot (a_{phy}^N \cdot C_{phy} + a_{dia}^N \cdot C_{dia} - \rho_{DON} \cdot f_T \cdot DON) + (18)$$
$$2(\lambda \cdot CaCO_{3det} - calcification)$$

here a_{phy}^N and a_{dia}^N are the nitrogen assimilation rates by phytoplankton and diatoms respectively and the remineralization of DON is represented by ($\rho_{DON} \cdot f_T \cdot DON$).

In this study, two fundamentally different set up of dissolution rate have been used. One is that λ (in equation 17 and 18) has been set in such a way that the dissolution happens all through the water column. In this case λ does not depend on saturation state but is described as a temperature dependent first-order dissolution reaction process [Yamanaka and Tajika, 1996]. Yamanaka and Tajika [1996] assume an exponential deacrese of the CaCO₃ sinking flux with depth, we reproduce this behaviour here by scaling λ with the sinking speed

$$\lambda = \lambda_0 \cdot \frac{w}{w(z=0)} \tag{19}$$

In the other run we made λ dependent on Ω . This dependency can be described by using the following equation

$$\lambda = \lambda_0 \cdot \begin{cases} (1 - \Omega) & \text{for } \Omega < 1\\ 0 & \text{for } \Omega > 1 \end{cases}$$
(20)

where λ = calcium carbonate dissolution rate and Ω = local saturation state

2.4 GLODAP data set

We make use of a high quality global $1^{\circ} \times 1^{\circ}$ gridded mapped climatology data product: version 2 of the Global Ocean Data Analysis Project (GLODAPv2) [Lauvset et al., 2016] that contains the primary biogeochemical variables total alkalinity (TA), total dissolved inorganic carbon (DIC), temperature, salinity, nitrate, oxygen, phosphate, silicate, *p*H, and also CaCO₃ saturation states (Ω). The data set is merged from 724 scientific cruises during the years 1972 to 2013 that cover all the ocean basins including the Arctic Ocean. The ocean depth is divided into 33 standard layers in this climatology.

3 Model - data comparison

3.1 Distribution of DIC and alkalinity from observational data and the baseline model run for the present day

Figure (5) shows the global dissolved inorganic carbon and alkalinity distribution at the ocean surface and at a depth of 3000 m from the GLODAPv2 data collection [Lauvset et al., 2016]. It is clearly seen from figure (5), that surface DIC has the lowest values near the equator and higher values towards the higher latitudes consistent with the higher solubility of CO_2 in cold water, but this feature is not completely uniform throughout the world ocean.



Figure 5: Global distribution of dissolved inorganic carbon and alkalinity from observational data (GLODAP data, 2016 [Lauvset et al., 2016]); first row of the image represent the DIC and alkalinity at the surface denoted by (a) whereas (b) denotes at 3000 m depth in the ocean.

The Pacific ocean surface has a lower value of DIC than the Atlantic and that fits with the fact that alkalinity is also slightly higher in the Atlantic Ocean surface. Alkalinity has maximum values in the subtropics surface ocean, where salinity is also highest, because of evaporation. Due to the high values of alkalinity in the subtropical ocean surface, DIC also has a maximum

there because with higher alkalinity, the ocean can store more carbon for the same atmospheric pCO_2 .

At 3000 m depth, in general both DIC and alkalinity concentrations are higher than at the surface. The reason behind this is the biological pump which moves DIC away from the surface ocean into the deep ocean. The biological pump also has a small effect on the alkalinity as well (because the remineralization of organic matter also releases nitrate (NO_3^{2-}) and phosphate (PO_4^{3-}) but these are small compared to the effect on alkalinity from formation and dissolution of CaCO₃. The dissolution of CaCO₃ releases alkalinity in the deep ocean, leading to the observed increase with depth. Starting from deep North Atlantic, we have the lowest values



Figure 6: Global distribution of dissolved inorganic carbon and alkalinity from model data set; first row of the image represent the DIC and alkalinity at the surface denoted by (a) whereas (b) denotes at 3050 depth in the ocean.

at depth both in alkalinity and DIC. As we follow the conveyor belt out of the Atlantic Ocean into the Antarctic Circumpolar Current and then into the deep Pacific Ocean, both DIC and alkalinity increase. Water there has lost contact with the atmosphere for the longest time so it has had the longest time to accumulate the remineralization products of organic carbon, and because of that DIC increases. Some dissolution of $CaCO_3$ also occurs here so there is also an

increase in alkalinity along the conveyor belt. However, the gradient is less strong in alkalinity than DIC because there is more organic carbon raining down than $CaCO_3$.

Figure (6) shows the global distribution of DIC and alkalinity from the model simulation. In general, the modeled data for DIC and alkalinity show quite similar patterns to the observational data, with low values at the surface and high in the deeper ocean. But the model data also shows some differences.

At the surface, the observational alkalinity in the South Atlantic and in the South Pacific seems to be slightly higher in the subtropics than in the model, especially in the southern hemisphere. At 3000 m depth, there is a strong gradient along the conveyor belt, with an increase along the conveyor belt both for DIC and alkalinity, so the general pattern is similar to observations. There is a difference in that the highest values in alkalinity in the deep ocean are found in the Indian Ocean in the model, while the maximum is distributed more broadly in the Indian and the Pacific Ocean for the observational data. This feature can be related to figure (8) from the masters thesis [Vhuiyan, 2016], where he found that the model has relatively high $CaCO_3$ export production in the Indian Ocean are caused by either a too low ventilation of this ocean basin or by a too strong calcification there.



Figure 7: Global average vertical profile of DIC from observational and model data; DIC form observational data denoted by (a) whereas (b) denotes the model data value.

In the case of DIC, it seems that the Atlantic values agree pretty well but that the increase

along the conveyor belt is a little bit weaker than in the observations. This pattern is similar for alkalinity values. Therefore the question is, what the reason behind this feature might be. Is it more a circulation feature or a feature of the biological production?

The export of organic carbon in the model is roughly 10 Pg C yr⁻¹ [Vhuiyan, 2016], which agrees with current estimates. So it is pretty clear that we do not have too little export of organic matter. Another reason could be that the distribution of remineralization over depth in the model differs from that in reality. The flux of organic carbon decreases with depth due to remineralization that happens while the organic particles sink, and we also do not know whether the model describes that very well or not.

Figure (5) and (6) represent the data only at the surface and at 3000 m depth, so from them we do not know anything what is happening in between. Figure (7) shows the global average



Figure 8: Global average vertical profile alkalinity from observational and model data; alkalinity form observational data denoted by (a) whereas (b) denotes the model data value.

vertical profile of dissolved inorganic carbon (DIC) from both observational and model data. It is clearly seen that in both, at the surface DIC is reduced and then increases with depth. In the observed data, the DIC increase with depth is strong in near the surface and decreases with depth; DIC gets almost uniform below 1500 m depth. In the model, there is an intermediate maximum where the dissolved inorganic carbon gets higher than the observations around 800 m to 1200 m depth. At depths larger than 2000 m, modeled DIC gets lower than observed. This is an indication that remineralization occurs too high in the water column and leads to an

overestimate at mid - depth and on underestimate at depth.

The global average vertical profile for alkalinity is shown in figure (8). Alkalinity values show similar features as DIC but much weaker with lower values near the surface with a small intermediate maximum and an increase with depth in between 1000 m to 4000 m. Surface values in the model are pretty close to observations, but also have a little bit too much increase in middepth around 1200 m to 2000 m. This might also be an indication that too much dissolution of CaCO₃ is happening at that depth range.

3.2 Saturation state of CaCO₃ from observational and model data

The saturation state of calcium carbonate (Ω) both from observational and model data are shown in figure (9) at the surface and at 3000 m depth. From this figure, it can be said that the saturation state of CaCO₃ is higher at the surface than in the deep ocean. At the surface it is high in the subtropical regions and lower towards the high latitude. These features are almost uniform all



Figure 9: Global distribution of saturation state (Ω) from observation and model data; first row of the image represent the value at the ocean surface denoted by (a) whereas (b) denotes at the deeper ocean.

over the world ocean. At 3000 m depth, the Atlantic Ocean shows slightly higher Ω values than the Pacific Ocean. The reason for this is that, along the conveyor belt the alkalinity increases not as much as DIC does (the alkalinity being always larger than DIC). So the difference between alkalinity and DIC is larger in the Atlantic than the Pacific. To a good approximation the difference between alkalinity and DIC is the concentration of CO_3^{2-} . So the carbonate ion concentration decreases from the Atlantic towards the Pacific as DIC increases.

Surface Ω value from the model simulation shows a higher value in the red sea and slightly higher value in the northern subtropical region of the Indian Ocean in comparison to observational data. In the deeper ocean, the model shows slightly higher values than the observations in the Atlantic Ocean and the Indian Ocean while the Pacific Ocean shows quite similar pattern.

The calculation of Ω should take into account that the nutrients like nitrate and silicate contribute to alkalinity. In this calculation, this contribution have been neglected because of the small effect on alkalinity [Orr and Epitalon, 2015]. The approximation that is used in this study for the calculation of Ω from DIC and alkalinity may create an error of Ω distribution in the deep ocean where nutrients are high. On the other hand, the surface ocean is not affected by nutrient concentration because here the nutrient concentrations are in general small except in the Southern Ocean.

4 Changes with LGM and present

To investigate the physical and biogeochemical changes between the LGM and present day, a model simulation for the LGM, with atmospheric forcing taken from coupled ocean-atmosphere simulations performed with COSMOS [Zhang et al., 2013], has been done (EXP 03). The simulation has come close to an equilibrium condition after 3000 years of integration time. Over the last 100 years of the integration time (years 2900 - 3000), average ocean temperature decreased by -0.01° C and the average ocean carbon content decreased by -0.441 μ mol/L.

4.1 Physical changes



4.1.1 Atlantic overturning circulation

Figure 10: Atlantic overturning streamfunction for LGM (a) and present day climate (b) and difference between them shown in figure (c).

The changes observed in the Atlantic ocean between the LGM and present day climate are connected to changes in the Atlantic meridional overturning circulation (AMOC) which is characterized by a northward flow of warm, salty water in the Atlantic upper layers to supply the formation of North Atlantic Deep Water (NADW), one of the primary overturning cells, and a southward flow of colder water in the deep Atlantic in which Antarctic Bottom Water (AABW) flows northward below depths of about 3,500 m and gradually rises into the lower part of the southward-flowing NADW [Delworth et al., 2008]. The Atlantic meridional overturning streamfunction for LGM and present day model runs are presented in figure (10). LGM AMOC is weaker and shallower than in the present day and has a maximum transport of 17.7 Sv for LGM where present day transport is 29.8 Sv. This is roughly consistent with the model results from [Völker and Köhler, 2013]. The weakened glacial AMOC is also associated with a shoaling of its lower boundary approximately from 3500 to 2000 m as Glacial North Atlantic Intermediate Water (GNAIW) due to the enhanced northward invasion of Antarctic Bottom Water (AABW). As a result, much of the Atlantic Ocean below 2000 m is dominated by Antarctic Bottom Water (AABW) as part of the lower overturning cell. These changes in the lower and upper overturning cells are conducive to the development of a global overturning circulation dominated by a denser AABW and a shallower AMOC. This shoaling depth of NADW is similar with [Buchanan et al., 2016b] where they mentioned that the the LGM NADW was lowered by approximately 3000 to 1500 m from the present day.

4.1.2 Atlantic zonal mean temperature and salinity

Figure (11) shows a meridional section of the zonal average temperature and salinity for both LGM and present day simulations and also the difference. Most of the Atlantic ocean in the LGM is cooler than at the present day. LGM NADW is getting much colder than the present day but AABW is not getting so much colder because it is already near freezing temperature.

On average the present day Atlantic ocean temperature is approximately 4° C higher than the glacial ocean. The LGM surface temperature ranges from approximately 23° C to -2° C while the present day surface temperature is from approximately 28° C to -1° C. The average surface temperatures are approximately 11° C and 14° C respectively. In the deep ocean, at 3050m depth, the LGM ocean temperature, range from approximately 0.23° C to -2° C where the present day temperature is from approximately 5° C to 0.1° C. The average deep ocean temperatures are approximately -1° C and 3° C respectively.

LGM salinity increases all over the ocean in the LGM because of less water in the ocean but the increases are not equally distributed. LGM Antarctic intermediate water remains relatively fresh and gets shallower but Antarctic Bottom Water gets saltier. The AABW becomes more salty in the LGM mainly due to the increase of the brine release associated with the formation of sea-ice.Antarctic Bottom Water forms under the regions of the year-round sea-ice cover. The corresponding sea ice growth and melting results in a vertically asymmetric redistribution of salt



Figure 11: Zonally averaged temperature (a and c) and salinity (b and d) and the difference in temperature(e) and salinity(f) within the Atlantic basin over LGM (a and b) and present day (c and d).

in ocean, transporting salt from surface to deep-ocean. These results agree with the pore fluid measurements reconstruction of the LGM temperature and salinity in sediment cores [Adkins et al., 2002].

In the present day ocean, both Antarctic intermediate water and Antarctic Bottom Water (AABW) are relatively fresh but the NADW is relatively more saline penetrating southward into the Southern Ocean and leading to a reversal of the salinity stratification in the abyss [Talley, 2013]. The associated overturning streamfunction (figure 10.b) reveals that this salinity feature is associated with NADW that flows southward as part of the Atlantic meridional overturning circulation (AMOC). Compared with LGM to present day, most of the regions are high in salinity except at the surface in the subtropics, caused by high evaporation in the subtropics. Atlantic LGM salinity is approximately 1 psu higher than the present day on average. Present day Atlantic surface salinity varies from 37.03 to 33.69 psu where LGM surface salinity ranging

from 37.70 to 32.83 psu. In the deep Atlantic, present day salinity values range from 35.67 to 35.01 psu where LGM maximum and minimum are approximately 37.38 to 36.4 psu.

4.1.3 Pacific zonal mean temperature and salinity

Zonal average Pacific Ocean temperature and salinity are shown in figure (12) both for LGM and present day. Temperature and salinity in the Pacific ocean shows a much more uniform pattern than the Atlantic ocean, especially a more cooling in the deep Pacific than the Atlantic because in the Pacific there is no Deep Water formation like in the Atlantic ocean. LGM pacific



Figure 12: Zonally averaged temperature (a and c) and salinity (b and d) and the difference in temperature(e) and salinity(f) within the Pacific basin over LGM (a and b) and present day (c and d).

deep water is cooler than at present day but the temperature difference is not that much as

surface because Pacific deep water is already much colder. North Pacific Intermediate Water (NPIW) is deeper in the LGM than in the present day which leads to the pattern of increased LGM temperature around 500 m depth in the upper North Pacific.

Modeled average LGM Pacific temperature is approximately 2° C lower than at the present day. But the lower thermocline in the North Pacific shows higher temperature for the LGM because of deeper NPIW whereas LGM Pacific averaged surface temperature is around 3° C cooler than at the present day. The LGM Pacific surface temperature ranges from approximately 25° C to -2° C where the present day surface temperature is from approximately 28° C to -1° C. Figure (12 b and d) shows the salinity in the Pacific ocean for the LGM and present day respectively. The Pacific deep ocean water for present and LGM climate show a similar trend i.e. both are more salty than the surface. But the LGM Pacific ocean is higher in salinity at the surface as well as at the deeper part than the present day. From the salinity difference plot between LGM and present day (figure 12.f), it is clear that the LGM Pacific ocean is more salty than the present day except some freshening of thermocline waters (AAIW and surface waters) in the south Pacific.



4.1.4 Maximum sea ice extent

Figure 13: Fractional sea ice cover maximum (September average) in the LGM (left) and present day (right).

The average sea ice extent for September over LGM and present day is presented in figure (13). Associated with colder sea surface temperature(SST), sea ice coverage (fractional sea ice area) is expanding in the LGM (for both hemispheres) compared to the present day. The

maximum sea ice-covered area is 33.7×10^6 km², more than twice the area in the present day simulation (11.9 × 10⁶ km²), and even in Southern hemisphere (SH) summer an area of 28.6 × 10⁶ km² remains ice covered, compared to only 0.8 × 10⁶ km² in the present day model simulation. During the LGM, the model produces a stronger seasonal cycle of sea ice area than at the present day. The northward expansion of sea ice around the Southern Ocean and Antarctica matches well with proxy reconstructions [Gersonde et al., 2005] and also with other model simulations [Buchanan et al., 2016a, Völker and Köhler, 2013]. Maximum sea ice extent ranged as far north as 47° S in both the Atlantic and Indian regions [Gersonde et al., 2005] and as far north as 55° S in the Southern Ocean Pacific region [Benz et al., 2016, Gersonde et al., 2005].

4.2 Biogeochemical changes

4.2.1 Atlantic zonal mean alkalinity and DIC

The Atlantic distribution of alkalinity and DIC for the LGM, present day and their difference are shown in figure 14. Both the LGM and present day simulations show a qualitatively similar pattern of alkalinity distribution with the lowest value found in southern hemisphere surface ocean and Antarctic Intermediate Water and highest value in the deep ocean. Both for the LGM and present day, deep Atlantic ocean has higher alkalinity concentration than the surface ocean. The lower alkalinity concentration in waters shallower than 500 m is resulting from the biological production of $CaCO_3$ while the higher alkalinity values in the deep ocean results from the dissolution of $CaCO_3$. The alkalinity distribution of the Atlantic ocean is also controlled by factors that govern salinity [Broecker and Peng, 1982, Millero et al., 1998].

In comparison to the present day, the LGM ocean is more alkaline at the ocean depth as it is more saltier than the present day (figure11.f). In the LGM, Antarctic bottom water (AABW) is getting more salty and also alkaline and NADW (less salty than AABW) is partly replaced by AABW. LGM alkalinity concentration is ranging approximately from 2690 to 2160 mmol/m³ where the present day ocean alkalinity concentration is from 2480 to 2283 mmol/m³. On average LGM ocean is higher in alkalinity concentration by approximately 45 mmol/m³. LGM Atlantic surface ocean has lower alkalinity concentration is about to 23 mmol/m³ whereas the deep ocean (3500m depth) is higher in concentration by approximately 115 mmol/m³ than the present day. A high alkalinity difference is observed at the deep Atlantic near 20° N caused by a more salty and isolated Caribbean sea.

In general, both the glacial and present deep Atlantic ocean is enriched in DIC compared



Figure 14: Zonally averaged alkalinity (a and c) and DIC (b and d) and the difference in alkalinity (e) and DIC(f) within the Atlantic basin over LGM (a and b) and present day (c and d).

to the surface ocean. For the present day, Antarctic Intermediate Water is relatively enriched in DIC partly because it comes from the Southern Ocean where DIC concentration is high and partly because of remineralization of organic matter. This tendency is getting stronger in the glacial ocean.

Glacial Atlantic oceanic concentration of DIC is on average approximately 24 mmol/m³ less than in the present day simulation. This carbon loss is probably related to the effect of physical changes in the ocean which include a number of effects that can have opposing effect on CO_2 like expansion of sea ice area, solubility increases due to cooling, overturning circulation change and the tendency of outgassing because of lower pCO_2 . Less concentration of DIC is observed in the LGM surface ocean because of lower pCO_2 at the LGM surface. The increase of DIC in deep water masses is associated with the replacement of relatively carbon poor NADW by carbon richer Antarctic bottom water.

Both LGM and present day ocean are also high in DIC at the equator in the depth between 500 to 1000 m because of the production of organic matter at the equator. The strength of this pattern has increased in the LGM ocean. Phytoplankton produces organic matter by the uptake of carbon dioxide, this organic matter is then transported to deeper layers and increases DIC when its remineralized at depth (biological pump).

Comparing the difference plot of alkalinity (14.e) and DIC (14.f), the LGM deeper ocean is generally high in alkalinity and DIC except for south of 60° S. In this latitude alkalinity increases but DIC decreases through the whole water column. One reason behind this decoupling is less biological production in high southern latitude in the glacial ocean and less organic carbon transport from the surface down deep into the ocean. Another reason is the lower glacial surface pCO_2 in general.

4.2.2 Pacific zonal mean alkalinity and DIC

Figure (15) shows the distribution of alkalinity and DIC in the Pacific Ocean for the LGM, the present day and also their differences. Both the LGM and present day Pacific Ocean show a qualitatively similar pattern of alkalinity and DIC distributions. Both LGM and present day Pacific Ocean alkalinity concentration at the depth ~ 0 to 1000m is lower than in the deeper ocean. Deep ocean alkalinity increases towards the North Pacific which contains the oldest water.

The DIC concentration is also generally lower in the surface than in the deeper ocean. Unlike for alkalinity, the maximum concentration of DIC in the North Pacific is found at intermediate water depths between 1000 - 2000 m. Both deep DIC and alkalinity are higher in the Pacific than in the Atlantic (both for LGM and present day) because they get enriched over time as deep water spreads Atlantic into the Pacific with the conveyor belt circulation.

In the present day, the lowest DIC and Talk concentrations in the Pacific are observed in surface waters. Surface DIC ranges approximately from 2236 to 1934 mmol/m³ where alkalinity varies from 2360 to 2159 mmol/m³. These variations in surface ocean carbonate concentrations are correlated with salinity. Circulation plays an important role to the distribution of DIC and alkalinity in the upper 1000m depth. Below North Pacific Intermediate Water (NPIW), alkalinity concentrations increase to a large maximum at approximately 1500 – 3500 m depth. Total alkalinity concentrations range from 2160 – 2474 mmol/m³. The differences between the DIC and alkalinity, especially in intermediate waters, are caused by in-situ re-mineralization. The DIC



Figure 15: Zonally averaged alkalinity (a and c) and DIC (b and d) and the difference in alkalinity (e) and DIC (f) within the Pacific Ocean basin over LGM (a and b) and present day (c and d).

maximum is shallower than the alkalinity because total inorganic carbon is influenced by the shallow re-mineralization of soft tissue organic matter, where the alkalinity is mostly influenced by the deeper calcium carbonate particles dissolution in the water column[Chen, 1990].

LGM Pacific ocean alkalinity and DIC concentrations are also qualitatively similar to the present day pattern i.e. low at surface and high at ocean depth. Most part of the LGM Pacific Ocean is quite substantially higher in alkalinity than in the present day except in AAIW, which is getting fresher (= less alkaline). DIC Pacific concentration in the LGM is higher in the deeper ocean and lower in the surface. DIC increases in the deep ocean below ~ 2500 m except in the Southern Ocean where it decreases while alkalinity increases. This pattern is similar to the pattern in the Atlantic.



4.3 Saturation state of CaCO₃ from LGM model run and difference between LGM and present day

Figure 16: Global distribution of saturation state (Ω) from LGM simulation and difference between LGM and present day: (a) and (b) represents the (Ω) from LGM simulation at the surface at 3050 m depth respectively whereas (c) and (d) denotes the difference between LGM and present day.

The global distribution of the saturation state of calcite from the LGM model run with uniform dissolution (EXP 03) and also the difference between LGM (EXP 03) and present day (EXP 01) model runs are shown in figure 16 at the surface and at 3050 m depth.

At the surface, LGM calcite saturation state is high in the subtropical regions (30° S - 30° N) and lower towards the high latitude. These features are almost uniform all over the world ocean. Qualitatively the global pattern of Ω does not change much at the depth of 3050 m. Figure 16 (c and d) represent the difference plot of CaCO₃ saturation state between LGM (EXP 03) and present day (EXP 01) respectively at the surface and in the deep ocean. The change between LGM and present day CaCO₃ saturation is higher at the surface than the deep ocean. LGM CaCO₃ saturation state is higher at the surface ocean. The increase LGM CaCO₃ saturation

state is uniform all over the world ocean with high value at the Atlantic and Pacific Ocean than the Indian Ocean. The Indian Ocean result is dominated by an apparent northward shift in low Ω Southern Ocean waters. Higher LGM surface ocean CaCO₃ saturation state can be explained by lower LGM *p*CO₂ that decrease LGM surface DIC concentration and also *p*H value goes higher and thus lead to increase Ω . As atmospheric CO₂ concentrations decrease, CO₂ concentrations in the surface ocean decrease as well, leading to an increase of the CaCO₃ saturation state in ocean surface [Zeebe and Wolf-Gladrow, 2001]. This is the inverse process of ocean acidification.

In the deep ocean (at 3050 m depth), the LGM Atlantic Ocean show the lower values than the present day while the Pacific and the Indian Ocean show the higher values. The alkalinity and DIC difference plot in the Pacific Ocean between EXP 03 to EXP 01 (figure 15.e and f) indicate that strong decrease of DIC in the surface and increase at the depth but not as much as alkalinity. So the concentration of CO_3^{2-} is higher at the deep Pacific which lead to higher CaCO₃ saturation state. The lower value of CaCO₃ saturation state in the deep Atlantic Ocean has to do with the higher carbon export mainly at the subtropics region.

4.4 Discussion

It is clearly observed from the description of chapter 4.2, that there are changes in the distribution of alkalinity and DIC between the LGM and present day model run both in the Atlantic and Pacific Ocean. Many factors can govern these changes: higher overall salinity and alkalinity of the ocean in the LGM changes, changes in the location of different water masses, changes in biological production, ocean temperature leading to changes in solubility of CO_2 , atmospheric pCO_2 etc.



Figure 17: Zonally averaged salinity normalized alkalinity within the Atlantic Ocean (a and c) and Pacific Ocean basin (b and d) between LGM and present day; (a and b) represent the salinity normalized alkalinity over LGM whereas (b and d) represent over present day and difference between them in the Atlantic shown by (e) and in the Pacific basin shown by (f).

To remove the effect of evaporation and precipitation (i.e. the hydrological cycle effect) a

salinity normalization on alkalinity (Alk₁) is done by converting each alkalinity (Alk) measurement to its expected value at a salinity (S) of 35 using equation (21) [Millero et al., 1998].

$$Alk_1 = \frac{Alk \times 35}{S}$$
(21)

The LGM and present day salinity normalized alkalinity (Alk_1) (fig 16. a – d) shows a similar pattern to the normal alkalinity (Alk) in the Atlantic (fig 14. a and c) and Pacific Ocean (fig 15. a and c) is lower at the surface and high at the deep ocean. The overall Alk₁ concentration is lower than the normal alkalinity (Alk).

The Alk₁ difference plot between LGM and present day Atlantic Ocean shows that the LGM Alk₁ concentration is lower at the depth range in between ~ 0 - 2000 m but higher at the deeper ocean than the present day. Also the whole water column south of 60 ° S shows a lower ALK₁ concentration. In the surface ocean, the distribution of Alk generally matches that of salinity because Alk in the open ocean is mainly controlled by salinity changes [Lee et al., 2006, Millero et al., 1998]. Maximum Alk₁ concentration in the Pacific Ocean is observed in the NPIW and the very most deeper ocean. The most northwestern part of NPIW is the freshest and most oxygenated part, suggesting that region is the source of NPIW for the subtropical gyre [Talley, 1993]. The LGM and present deep Atlantic and Pacific Ocean chemistry can be distinguished



Figure 18: Sinking flux of particulate organic carbon (POC) over 100 m depth for the LGM (a) and present day (b) and the difference between them shown in (c).

from each other by the formation of freshly ventilated deep water in the present day North

Atlantic Ocean, which was more homogeneous during glacial time [Lea, 1993, Boyle, 1992, Duplessy et al., 1988, Curry and Lohmann, 1982]. From the salinity normalized alkalinity plot one can see that the location change of different water masses is an important factor. Along with the location change of different water masses between LGM and present day their salinity also changes. The most prominent example is the larger volume of AABW in the Atlantic which at the same time gets saltier.

The lower surface Alk_1 is governed by the production of $CaCO_3$ where the deeper high concentration Alk_1 is dominated by the dissolution of $CaCO_3$. $CaCO_3$ is produced at the surface ocean and starts to dissolve when it leaves the productive upper layers of the ocean as upper layer is supersaturated with respect to both mineral phase of $CaCO_3$.

The overall Alk_1 distribution shows that an important factor in the change of ALK is the extended volume of AABW in the LGM. But the decrease of Alk_1 in the upper 2000 m and throughout the water column in the Southern Ocean as well as the increases of Alk_1 below 2000 m in the rest of the ocean point to changes in the vertical flux of POC and CaCO₃ as further factors. Figure 18 and 19 shows the sinking flux of POC and CaCO₃ and also the differences



Figure 19: Sinking flux of calcium carbonate $(CaCO_3)$ over 100 m depth for the LGM (a) and present day (b) and the difference between them shown in (c).

between LGM and present day. The LGM POC export is higher mainly in the tropical region of the Atlantic Ocean, at the east equatorial and northern subtropics of the Pacific Ocean. The

subtropical regions are oligotrophic i.e. nutrient poor so that there is not much export of organic carbon. Enhanced productivity is also detected in the subpolar regions in the Atlantic and the North Pacific, around Antarctica and throughout the north Indian Ocean mostly driven by diatoms. The overall calculated POC export (6.830 Pg C yr⁻¹) is lower in the LGM than the present day (9.647 Pg C yr⁻¹).

The maximum CaCO₃ export mostly occurs at the boundaries between high nutrient and low nutrient conditions, e.g. at the boundaries of equatorial upwelling. The subpolar regions, where much POC export happens, are regions of less CaCO₃ export. The maximum export of CaCO₃ is found in the Indian Ocean. LGM CaCO₃ export also higher at the tropical region of Atlantic Ocean, eastern equatorial Pacific Ocean than the present day. The glacial model run calculates a total export of CaCO₃ of 0.281 Pg C yr⁻¹ which is lower than the present day $(0.342 \text{ Pg C yr}^{-1})$.



Figure 20: Zonally averaged differences in dissolved inorganic nitrogen (DIN) within the Atlantic (a) and Pacific basin (b) over LGM and present day.

The change of POC export is also reflected in the dissolved inorganic nitrogen (DIN) distribution differences (figure 20). Figure 20 shows the difference in dissolved inorganic nitrogen (DIN) between the LGM and present day over the Atlantic and Pacific Ocean. The mid depth changes in DIC are quite similar to changes in DIN distribution. This suggest that they are driven by a high biological production with more export of organic carbon in the tropical Atlantic and less export in the Southern Ocean.

5 Changes due to omega (Ω) dependency to calcite dissolution

Two further model simulations (EXP 02 and EXP 04, table 1) with a dependency of dissolution of CaCO₃ on the saturation state (Ω) have been done for present day and LGM. The aim is to see how alkalinity, DIC and saturation horizon vary from the previous model runs where dissolution was not dependent on Ω . Between model runs EXP 01 and EXP 02, and between EXP 03 and EXP 04 the only thing that changes is CaCO₃ dissolution. Changes in CaCO₃ dissolution will not affect the physics of the ocean and the biological production. Only DIC, alkalinity and saturation state will be changed. In this chapter, therefore only the changes in DIC, alkalinity and associated Ω are discussed.

5.1 Present day



Figure 21: Global average vertical profile of DIC and alkalinity from observational and model data (with and without Ω dependent dissolution); DIC profile denoted by (a) whereas (b) denotes the alkalinity.

Figure 21 shows different global average vertical profiles for DIC (figure 21.a) and alkalinity (figure 21.b) obtained from the GLODAP and present day model simulations with (EXP 02) and without (EXP 01) Ω dependent dissolution. In case of DIC and alkalinity, the difference

between observational data and model simulation (EXP 01) that is observed at mid depth has been discussed briefly in chapter 3.1 (figure 7 and 8).

Comparing EXP 02 to EXP 01 there are some differences in DIC and alkalinity which are stronger near the surface ocean. Alkalinity from EXP 02 is on average higher by approximately 5.22 micromol/kg than the alkalinity from EXP 01 and the surface value is higher by around 12.55 micromol/kg. The difference increases from the surface to 800 m depth and then starts to decrease after-that. This pattern is same for DIC. DIC from EXP 02 is higher on average by approximately 4.9 micromol/kg than the values from EXP 01 and the surface value is higher by around 13.65 micromol/kg.



Figure 22: Distribution of alkalinity difference from model data (uniform dissolution - Ω dependent dissolution) at the surface and 3050 m depth.

The horizontal distribution of alkalinity difference between uniform and Ω dependent dissolution model run is shown in figure 22 at the surface and 3050 m depth. From the figure 22, it is clear that the surface alkalinity from EXP 01 is lower all over the world ocean than the alkalinity from EXP 02. The equatorial Pacific and Indian Ocean shows strong increasing pattern than the Atlantic and Southern Ocean. At the depth of 3050 m, the difference pattern does not have a uniform sign all over the ocean. The alkalinity concentration from the Ω dependent dissolution model run is higher in the Atlantic and Southern Ocean while the Pacific north of 30° S and Indian Ocean show lower alkalinity concentration.

As alkalinity and DIC change with the changes of dissolution rate, ocean saturation state (Ω) also changes. Figure 23 shows the global distribution of the saturation state (Ω) of calcite from the two different model runs EXP 01 and EXP 02 at the surface and at 3050 m depth and also their differences. The saturation state of CaCO₃ is higher in both runs at the surface than in the deep ocean.



Figure 23: Global distribution of saturation state (Ω) of calcite from model data (uniform and Ω dependent dissolution and also their differences at the surface and at 3050 m depth; (a and b) represent the value from uniform dissolution whereas (c and d) denotes Ω from Ω dependent dissolution model run, (a and c) for the surface and (b and d) at 3050 m depth, surface difference shown by (e) where (f) represent difference at 3050 m depth.

The surface distribution of Ω from two different model run shows qualitatively similar patterns, high in the subtropical regions and lower towards the high latitude. These patterns are almost uniform all over the world ocean. From the surface Ω difference plot (uniform dissolution – Ω dependent dissolution) it is obvious to say that Ω from uniform dissolution is higher all over the world ocean except the Southern Ocean. Surface Ω value from run EXP 01 shows a higher value in the red sea, a slightly higher value in northern high latitude of Atlantic Ocean in comparison to model simulation EXP 02 with Ω dependent dissolution.

At 3050 m depth, Ω value from EXP 01 and EXP 02 also shows the similar pattern with

higher Ω values in the Atlantic Ocean than the Pacific Ocean. The reason for this is that the carbonate ion concentration decreases from the Atlantic towards the Pacific as DIC increases. The difference between alkalinity and DIC is larger in the Atlantic than the Pacific because along with the conveyor belt the alkalinity increases not as much as DIC. In the deeper ocean, Ω from run EXP 01 with uniform dissolution shows slightly higher values than with Ω dependent dissolution in the Atlantic Ocean approximately in between 45° S – 45° N and some subtropical parts of the Indian Ocean while the Pacific Ocean shows a quite similar pattern.



Figure 24: Global average vertical profile of saturation state (Ω) of calcite (dimensionless) from observational and model data(with and without Ω dependent dissolution).

Figure 24 shows the global average vertical profiles for Ω obtained from the GLODAP.v2 observational data and from the simulations with and without dissolution dependency on Ω . Both model profiles show a decrease with depth with an intermediate minimum at around 800 m depth, while the data based profile shows only a decrease. This is probably due to the too strong remineralization at that depth also evident in the DIC profile (figure 21.a). The global average vertical profile of Ω from model simulation EXP 02 is much closer to the observational data than the Ω from EXP 01 showing that this parameterization improves the model results.

6 Summary and discussion

The research presented in this thesis deal with changes in CaCO₃ dissolution in the LGM and present ocean. CaCO₃ dissolution changes is related to the degree of ocean saturation state that is further linked to the oceanic distribution of alkalinity, DIC, salinity and temperature etc. To analyze the changes, four different model simulations have been done: two for the present day and another two for the LGM. At first, one baseline model simulation for the present day has been done with uniform dissolution and results have been compared to the observational data (GLODAP.v2). Global distribution of surface and deep ocean alkalinity and DIC from the baseline simulation show a qualitatively similar pattern to the observational data with a low value at the surface and high in the deeper ocean. Compared to model data, the surface observational alkalinity in the South Atlantic and in the South Pacific seems to be slightly higher in the subtropics. There is a difference in that the highest values in alkalinity in the deep ocean are found in the Indian Ocean in the model, while the maximum is distributed more broadly in the Indian and the Pacific Ocean for the observational data. This feature can be related to figure 19 where the model has relatively high $CaCO_3$ export production in the Indian Ocean. The average vertical profiles of alkalinity and DIC, when compared to GLODAP.v2. (figure 7 and 8) show that there is too much remineralization in the water column at the lower thermocline (~ 1000 m depth) and too high CaCO₃ dissolution is happening at intermediate depths.

The LGM model simulation has been done with atmospheric forcing taken from coupled ocean-atmosphere simulations performed with COSMOS [Zhang et al., 2013] to investigate the physical and biogeochemical changes between LGM and present day excluding however the effect of iron fertilization.

The model simulation under the glacial boundary conditions simulates a saltier and cold ocean than at present day. The main changes in oceanic circulation are associated with a shoaling and a weakening of the Atlantic meridional overturning cell and increase of Antarctic Bottom Water formation with a much stronger penetration of AABW into the Atlantic Ocean. In the present day AABW is present only in the Atlantic at the below 3000 m depth (figure 10.b), while glacial AABW fills the entire Atlantic basin below 2000 m (Figure 10.a). The resulting shoaling and weakening of the Atlantic meridional overturning is consistent with many other model simulations [Buchanan et al., 2016b, Völker and Köhler, 2013, Zhang et al., 2013, Brovkin et al., 2007].

The change in simulated sea surface temperature (SST) between LGM and present day shows the greatest cooling in the equatorial region, and high latitudes and the least cooling in the subtropics. The mean LGM SST was 2.7° C cooler than for the present day. This change falls within the range of estimates (~ 2-4° C) produced by other climate models [Alder and Hostetler, 2015, Annan and Hargreaves, 2013, Braconnot et al., 2007]. The average Atlantic LGM ocean temperature is cooler by 3.8° C and the Pacific LGM is cooler by 2.1° C than the present day.

The overall LGM salinity is higher than the present day because of lowering of sea level by 116 m. The larger winter sea ice extent and the northward shift of summer sea ice extent increase the sea ice transport out from the AABW formation area, which increases the salinity of AABW and decreases surface salinity in the subtropical Atlantic Ocean. The simulated increase of AABW salinity is consistent with [Adkins et al., 2002].

A comparison of the alkalinity and DIC concentration in the LGM model run (EXP 03) with the present day run (EXP 01) shows the influence of several factors. From the salinity normalized alkalinity plot (figure 17), it is clear that the changes in salinity and also the changes in the location of different water masses play a vital role in the distribution of alkalinity. The larger volume of saltier AABW in the LGM Atlantic Ocean is the most prominent example of changes in the location of different water masses. Changes in the vertical flux of POC and CaCO₃ act as further factors (changes in biological production) to explain the decrease of salinity normalized alkalinity in the upper 2000 m and throughout the water column in the Southern Ocean as well as the increases of salinity normalized alkalinity below 2000 m in the rest of the ocean.

The mid depth changes in DIC between LGM and present day are quite similar in pattern to changes in DIN distribution. This suggest that they are driven by a high biological production with more export of organic carbon in the tropical Atlantic and less export in the Southern Ocean.

Two new model simulations (EXP 02 and EXP 04) with a modified dissolution rate (Ω dependent dissolution) for the LGM and present day have been done to see how alkalinity, DIC and saturation horizon vary from the previous model runs with uniform dissolution. But the run for glacial climate experienced problems from the convergence of the calculation of pCO_2 from DIC and alkalinity that was therefore not analyzed further. Compared to global observation (GLODAP.v2), Present day Ω dependent dissolution model simulation provides a better DIC and alkalinity profile than the uniform dissolution present day simulation (EXP 01) with a discrepancy at the mid depth. The difference in alkalinity from global observation to Ω dependent dissolution is around 4.8 micromol/kg where this difference is higher by ~ 10.1 micromol/kg from global observation to uniform dissolution.

Associated with the change in DIC and alkalinity, ocean saturation state also changes. The Ω from both model run shows qualitatively similar pattern with the observational data: decreasing along with depth with an intermediate minimum at around 800 m depth, while the data based profile shows only the decrease. The global average vertical profile of omega from Ω dependent model simulation is much closer to the observational data (with difference is only around 0.13) than the Ω from uniform dissolution model run (difference is around 0.48) showing that this parameterization improves the model results.

7 Conclusion

The production of calcium carbonate production in oceanic surface waters and its dissolution or accumulation in sediments has a direct effect on the concentration of dissolved inorganic carbon and alkalinity and thus influences the oceanic uptake capacity of atmospheric CO₂ by determining the surface water CO₂ concentration. In this study, modeled saturation state and DIC and alkalinity concentrations have been compared with observational data. The saturation horizon is directly related to the oceanic content of DIC and alkalinity. Comparing the model simulation with the observation, the general pattern for DIC, alkalinity and for Ω values are quite similar. Increased DIC concentration in the water column at the lower thermocline (~ 1000 m depth) indicates too much remineralization at that depth while high alkalinity concentration at the intermediate depth indicates too high CaCO₃ dissolution.

Compared to the present day model, a model simulation under glacial boundary conditions simulates a more saltier and less cooler ocean than the present day. The main changes in oceanic circulation are associated with a shoaling and a weakening of the Atlantic meridional overturning cell and an increase of Antarctic Bottom Water formation with a much stronger penetration of AABW into the Atlantic Ocean. Distribution of alkalinity, DIC and associated saturation horizon of the ocean are also changed with the change of atmospheric forcing from present to glacial climate. The overall LGM salinity and nutrient concentration is higher than the present day because of lowering of sea level by 116 m. LGM alkalinity concentration is lower at the depth range in between $\sim 0 - 2000$ m but higher at the deeper ocean than the present day. The surface alkalinity changes are driven by the salinity changes along with the location changes of different water mass between LGM and present day. Increases of salinity normalized alkalinity below 2000 m in the ocean point to changes in the vertical flux of POC and CaCO₃ as further factors.

In this study, it is tested whether an improvement in the modeled alkalinity, DIC and saturation state (Ω) distribution can be reached by making the dissolution depends on the CaCO₃ saturation state. It is shown that the making calcite dissolution depend on the CaCO₃ saturation state gives much more improved distribution of alkalinity, DIC and saturation state (Ω) that is much closer to the observational data.

One aspect which has been not studied in this study is the effect of iron fertilization. LGM model simulation has been done with the same dust deposition of present day although glacial time dust deposition was stronger because of dryer atmosphere and more exposed shelves. This would be the obvious thing to look at next.

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