



An Investigation of the Geoengineering Possibilities and Impact of Enhanced Olivine Weathering

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Declaration

I, Jesse Abrams, herewith declare that I did the written work on my own and only with the means as indicated.

Signature

Date

J. Abrams

Abstract

Geoengineering methods are being explored to counteract global warming effects on Earth's climate. The use of enhanced silicate weathering has been proposed as a method that could speed up the consumption of CO₂ by enhancing naturally occurring chemical weathering. This study investigates that method, which involves grinding, dispersing and dissolving olivine, a magnesium silicate mineral, in river catchments and over the open ocean in order to absorb excess CO₂ and oppose ocean acidification. Previous research shows that if olivine is distributed over land areas of the tropics, it has the potential to sequester as much as 1 Pg C yr⁻¹ [Köhler et al., 2010]. Olivine distribution over the open ocean has the potential to further increase the sequestration of carbon. Here, I explore different distribution scenarios of olivine into the ocean using the REcoM-2 biogeochemical model coupled to the MITgcm ocean general circulation model.

The additional distribution of finely ground olivine over the open ocean results in an increase in the amount of carbon sequestered and lowers the sea surface pCO_2 . In this study, I calculate the additional flux of CO_2 into the ocean to be approximately 0.8 Pg Carbon Dioxide per Pg olivine, which is lower than previous findings and lower than the expected value. Additionally, the higher availability of silicate due to olivine dissolution creates better growing conditions for large silicon dependant diatoms causing a decline in small phytoplankton biomass and an increase in diatom biomass. This leads to an increase in primary production due to improved conditions for diatoms. The pattern of export production was expected to correlate to the pattern of primary production, with an increase in primary production leading to an increase in the amount of carbon exported to the deep ocean. The results show that the opposite effect actually happened, with carbon export decreasing as olivine flux increased. This decrease in export production can be attributed to the decrease in small phytoplankton as calcifiers play a very important role in the export of carbon. While the change the CO₂ flux into the ocean due to the change in ocean biology is highly non-linear and responsible for little change in the, the change in ocean chemistry scales linearly and leads to a significant change. The change in alkalinity is responsible for the majority of the effect of olivine dissolution and leads to an increase in CO₂ flux by approximately 0.2 petagrams carbon per petagram of olivine.

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I also explore the possible side effects, both wanted and unwanted, of enhanced weathering. These include a significant shift in the phytoplankton communities in favor of diatoms, the rise in pH leading to a reversal of ocean acidification, and other important questions such as the possible generation of anoxic areas and the outgassing of more serious greenhouse gases.

As one of the least expensive geoengineering methods, enhanced weathering is a promising option to help contribute to the efforts to reduce the effects of climate change. However, this can cause both intentional and unintentional changes to the climate that may have potentially important consequences on the Earth's ecosystem.

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Chapter 1: Introduction

1.1 General Introduction and Motivation

The Earth's climate has experienced inordinate global change due to anthropogenic influence. Due to anthropogenic input, the atmospheric CO₂ concentration has increased from 280 parts per million (ppm) CO₂ during preindustrial times to about 390 ppm today. The release of excess carbon dioxide (CO_2) and other greenhouse gases promotes global temperature increases that exceed changes that would be expected due to natural variability [Allen et al., 2009; Meinshausen et al., 2009]. The increase in CO₂ in the atmosphere has also led to other adverse effects such as the acidification of the Earth's oceans and other surface waters. The problems associated with accelerated warming will continue to worsen as CO₂ levels increase beyond the capacity of ecosystems to adapt. The Earth's natural processes help dampen the effect of the anthropogenic CO₂ released, but cannot keep pace with the anthropomorphic amplification of natural processes [Archer, 2010; Gruber et al., 2009]. As CO₂ levels increase, the ability of the natural sinks to absorb CO₂ will deteriorate faster than living resources can tolerate, leading to species loss, and ecological community collapses [Allen et al., 2009; Meinshausen et al., 2009; Solomon et al., 2009; Smith et al., 2009].

In order to stay below the goal of 2 degree Celsius increase that was set by the UNFCC, we must stabilize the level of atmospheric CO_2 below 450 ppm. According to Solomon this requires a 30% to 85% net reduction in CO_2 emissions by 2050 [IPCC, 2007]. Since such a huge reduction in our dependence on fossil fuels is not feasible any time soon, methods to reduce the amount of carbon in the atmosphere must be considered [IPCC, 2007].

It is necessary to explore realistic ways to ameliorate global climate change. There exist two options to prevent further damage: mitigation and geoengineering [IPCC, 2007; IPCC, 2001]. Mitigation refers to the reduction of, or compensation for anthropogenic emissions, as addressed in the United Nations Framework Convention on Climate Change (UNFCCC), in order to manage dangerous climate change [United Nations (1998)]. Alternatively, there have been various geoengineering concepts proposed to counteract global warming [Lenton & Vaughan, 2009; The Royal Society, 2009]. Geoengineering, in general, refers to any method that intentionally alters the Earth's climate.

This thesis will investigate a specific geoengineering technique, the sequestration of carbon through the artificially enhanced silicate of olivine. This technique is able to mitigate the auxiliary problems discussed above, global warming and ocean acidification. In this study, the efficiency of one method of carbon sequestration and the ecological impacts on the marine ecosystem will be explored. The proposed mechanism consumes CO_2 during the weathering reaction. Additionally, it increase alkalinity and has the potential to enhance the biological pump by providing large-scale inputs of silicate for use by diatoms, silicate-based phytoplankton that out compete other phytoplankton when silica is present in the surface waters. Since in general the supply of silica is limited, the excess silica will promote enormous growth in diatoms, thus removing CO_2 as these organisms' bioprocessing consume it from the surface ocean waters. However, there may be unknown consequences on other the marine ecosystem, and the biological and carbonate pumps.

In a recent review conducted by the Royal Society the options for fighting global warming with geoengineering were evaluated [The Royal Society, 2009]. Artificial weathering was viewed as one of the most promising ways to reduce carbon levels [The Royal Society, 2009; Brumfiel, 2009]. The Royal Society (2009) also pointed out that this method is not fully understood and requires more study. Köhler et al. (2010) have recently evaluated the potential of enhanced silicate weathering on land as a geoengineering option, but this research left many questions.

This research is based on the work of Köhler et al. (2010), which explored the potential of silicate weathering on land. In this thesis, I plan to extend the research to explore the potential of distributing olivine in the open ocean. The goal of this research is to investigate the efficiency of carbon capture via enhanced silicate weathering and the intended and unintended consequences of enhanced olivine weathering as a possible geoengineering method. Key questions in this study are:

- 1. What is the impact of additional weathering on silicic acid (Si(OH)₄) distribution in the oceans?
- 2. What is the response of marine biota (especially diatoms versus nondiatoms), biological production and export to additional silicic acid?
- 3. What are the impacts of the additional silicic acid and alkalinity on nutrients and the marine carbonate system?
- 4. What are the impacts of olivine weathering on ocean acidification?

To explore this, the MITgcm (MIT General Circulation Model) coupled with the REcoM-2 pelagic ecosystem model will be used. The MITgcm is a general circulation model (GCM) that represents oceanic flow on a three dimensional grid with velocities, temperature, CO₂ concentration, nutrient concentration, and other variables stored at each grid point [Matter & Kelemen, 2009; MITgcm, 2002]. The REcoM-2 (Regulated Ecosystem Model) is an ecosystem model based on a model for phytoplankton adaptation to changes in light and nutrient availability [Geider et al., 1998]. The impact of olivine weathering on carbon levels is investigated on a five-year timescale and therefore no sediment model is required because the impact on sediment is seen only on larger timescales [Matter & Kelemen, 2009]. The model is initially used to examine different ocean input scenarios.

1.2 Climate Change Energy Balance and Geoengineering

Energy Balance

All geoengineering techniques aim to alter the Earth's climate by altering the Earth's radiation balance. For this reason, it is essential that this research reflects a basic understanding of the Earth's radiation balance (Fig. 1). All significant exchange of energy between the Earth and the rest of the universe is by way of radiation, and the energy received from the sun is the dominant energy source driving all processes on the Earth surface. There is a constant flow of energy from the Sun to the Earth and back into space, resulting in a rather stable mean temperature on Earth.



Figure 1: Details of Earth's radiation budget (all numbers shown have units of Wm⁻²) [Source: Kiehl and Trenberth, 1997].

The average amount of radiation from the Sun, in the form of visible light and infrared radiation, reaching the top of Earth's atmosphere is around 342 W/m^2 [Wallace & Hobbs, 2006]. The Earth absorbs less than half of this sunlight, with the rest being reflected back to space or absorbed in the atmosphere. The percentage of solar energy that is reflected back to space is called the albedo, which is dependent on the surface type, with an average of 0.30 (which corresponds to about 30 percent of the incoming solar energy being reflected) on Earth [Wallace & Hobbs, 2006].

The solar radiation that makes it to the Earth's surface is absorbed and heats the Earth. Since any object that has a temperature emits energy, the Earth emits its own form of energy as well. The warm surface of the Earth emits long wave, infrared radiation, which we feel as heat. Some of the heat escapes to space, while some of the radiation is absorbed by gases, such as CO₂, present in the atmosphere and reradiated back towards the Earth, leading to further warming of the Earth's surface. This natural warming process is known as the greenhouse effect [Wallace & Hobbs, 2006]. Without the Earth's natural greenhouse effect the planet would be too cold to sustain human life [Wallace & Hobbs, 2006].

Climate Change

The combustion of fossil fuels (8.7 PgC/yr) and clearing of land (1.6 PgC/yr) [Matter & Kelemen, 2009] takes carbon that was essentially dormant and releases it into the atmosphere [Archer, 2010], creating the increases in CO_2 being observed. In the atmosphere, the additional CO_2 has altered the atmospheric chemistry increasing the greenhouse effect. Additionally, the ocean is known to absorb about 30% of the extra atmospheric CO_2 . Oceanic uptake of atmospheric CO_2 released by humans is altering seawater chemistry leading to negative impacts on marine biota, ecosystems and biogeochemistry [Doney et al., 2009]. The Intergovernmental Panel on Climate Change (IPCC) projects that if CO_2 emission rates continue to increase at the present rate then the atmospheric CO_2 levels of about 800ppm or more by the year 2100.

Carbon dioxide can be found in the air, dissolved in water or stored in sediments. Even though carbon dioxide is present in small quantities in the Earth's atmosphere, it is more important in the Earth's radiation balance than more abundant gases such as oxygen (O_2), nitrogen (N_2), and argon (Ar) due to its molecular structure.

The structure of carbon dioxide allows additional transitions through the possibility of rotation and vibration. There are less rotational and vibrational bands in

 N_2 and O_2 (only two atoms) and none in Ar. The frequencies of absorption are determined by the vibrational and rotational modes [Archer, 2010]. The absorption band of interest for climate warming in CO_2 is the band that occurs near 700 cm⁻¹ because this occurs with the peak of IR [Archer, 2010]. This is why the radiative forcing from CO_2 is of great interest [Archer, 2010].



Figure 2: Radiative transfer in Earth's atmosphere [Source: IPCC, 2007].

The radiative forcing contribution from carbon dioxide is the greatest among the gases that are long-lived in the atmosphere (Fig. 2). Because of this characteristic, it has an exceptionally important role in the energy balance of the Earth; an increase in the concentration of CO_2 means that more heat is captured.

Geoengineering

Geoengineering is defined as the large-scale engineering of our environment in order to combat or counteract the effects of human-induced climate change, addressing in particular the negative effects associated with elevated levels of greenhouse gases [Lenton & Vaughan, 2009; The Royal Society, 2009].

Several methods of geoengineering exist (Fig. 3 & 4), falling into one of two classes: Carbon Dioxide Removal (CDR) techniques and Solar Radiation Management (SRM) techniques [The Royal Society, 2009; Köhler et al., 2010]. While the goal of both of these techniques is to reduce global temperatures, they approach the problem in different ways.



Figure 3: Schematic representing various geoengineering proposals [Source: B. Matthews].



Figure 4: Schematic illustrating how SRM aims to alter the Earth's albedo while CDR aims to remove carbon dioxide from the atmosphere [Source: The Royal Society, 2009].

Carbon Dioxide Removal (CDR) techniques directly remove CO₂ from the atmosphere and thus address the root of the climate change problem and not just the effects [Köhler et al., 2010; Lackner, 2002; Lackner, 2003; Stephens & Keith, 2008]. Carbon sequestration involves the use of reservoirs, ocean water, ageing oil fields, or other carbon sinks to absorb excess carbon. Some carbon dioxide is naturally absorbed through physical, chemical, or biological processes by various carbon sinks. CDR techniques aim to exploit these natural sequestration processes [Lackner, 2003; Keith et al., 2006].

Solar Radiation Management (SRM) techniques aim to reduce the warming of the planet by directly modify the Earth's radiation balance by artificially increasing the planet's albedo [Crutzen, 2006; Caldeira & Wood, 2008]. Although SRM techniques would help mediate the effects of climate change, they do not address the root cause. Furthermore, they do not help with any of the additional problems such as ocean acidification [The Royal Society, 2009]. SRM techniques do have the advantage of speed and would take only a few years to have an effect on climate once deployed and could be useful in an emergency, for example to avoid reaching a climate 'tipping point' [Lenton & Vaughan, 2009; Archer, 2010].

1.3 The Global Carbon Cycle

Carbon Fluxes and Reservoirs

The carbon cycle is the complex biogeochemical cycle by which carbon is exchanged throughout the climate system by biological, chemical and physical processes [Archer, 2010]. Carbon in the form of CO₂ is constantly exchanged between the atmosphere and the other components of the climate system. Carbon dioxide in the Earth's atmosphere is the most significant source of global warming and even though the carbon has a large effect in the atmosphere, it makes up a relatively small percentage of the atmosphere [Wayne, 2000]. The Earth's approximate atmospheric composition is shown in Table 1.

Atmospheric Component	% Volume
N ₂	78
O ₂	21
Ar	0.9
H ₂ O	<1
CO ₂	0.039
CH ₄	0.00017

Table 1: Composition of Earth's atmosphere [Source: Wayne, 2000].

Carbon dioxide occurs as a trace constituent in the atmosphere, composing about 0.039% of the total composition of the atmosphere at present [Wayne, 2000]. The total amount of carbon in the Earth's atmosphere is about 825 PgC. The atmosphere is only the fourth largest reservoir out of the five components of the climate system, but it is important in the carbon cycle because the other reservoirs interact with each other mainly by trading carbon with the atmosphere [Gruber et al., 2009].

The ocean is the second largest reservoir for carbon, but has the largest active pool of carbon near the Earth's surface [Siegenthaler & Sarmiento, 1993]. The Earth's oceans contain about 38,000 PgC of dissolved inorganic carbon, which is about 50 times the amount of carbon in the atmosphere. The oceans have an additional 3 PgC in organic biomass [Siegenthaler & Sarmiento, 1993; Eswaran &

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Reich, 1993; Hedges, 1992; Schimel, 1995]. Most of the carbon in the Earth's oceans is found in inorganic forms: dissolved CO_2 , carbonic acid (H₂CO₃), bicarbonate ion (HCO₃⁻), and carbonate ion (CO₃⁻) [Ruddiman, 2001].

Table 2: Summary table of global carbon pools [Source: Siegenthaler & Sarmiento, 1993; Eswaran & Reich,1993; Hedges, 1992; Schimel, 1995].

Global C pools	Pg C	% total
Lithosphere	75011150	99.94
Limestone	6000000	79.94
Kerogen	1500000	19.99
Methan clathrates	11000	0.01
"active" sediments	150	0.00
Ocean	39200	0.05
Organic C	1078	0.00
Living	3	0.00
Dissolved carbonate	38000	0.05
Soils	1580	0.00
Peat	360	0.00
Microbial	15-30	0.00
Intermediate	250-500	0.00
Slow	600-800	0.00
Atmosphere	750	0.00
Terrestrial Plants	610	0.00
Totals	75053290	

The other three reservoirs are the lithosphere (rocks), the land (vegetation), and the soil. The lithosphere is the largest reservoir containing 7.5×10^7 PgC [Siegenthaler & Sarmiento, 1993; Eswaran & Reich, 1993; Hedges, 1992; Schimel, 1995]. The lithosphere is by far the largest reservoir, but only a small portion is near the surface, therefore the exchange with other parts of the climate system is slow. The mean biomass of carbon in vegetation varies between $0.3 \text{ kg} \cdot \text{C} \cdot \text{m}^{-2}$ in deserts to $15 \text{ kg} \cdot \text{C} \cdot \text{m}^{-2}$ in tropical rain forests [Eswaran & Reich, 1993; Hedges, 1992; Schimel, 1995]. About 610 PgC exists in all terrestrial vegetation; this is the only reservoir that contains less carbon than the atmosphere. Carbon in soil is present in different amounts in different types of land, with a total of 1,580 PgC in all of the Earth's soils, which is double the amount of carbon present in the atmosphere [Eswaren & Reich, 1993].



Figure 5: The major reservoirs of carbon in Gt and the major fluxes in GtC/yr [Source: The Royal Society, 2009].

Carbon Dioxide Exchange and the Carbonate System

The air-sea interface is a unique environment through which pass gasses, and measurement of this flux is important. The amount of a gas that is soluble in a liquid follows Henry's Law:

$$c = k_H \cdot pCO_2$$
 [1.1]

where *p* is the partial pressure of the solute in the gas above the solution, *c* is the concentration of the solute and k_H is a constant, known as the Henry's Law constant, which depends on the solute, the solvent and the temperature.

The oceans have a strong influence on the CO_2 concentration in the atmosphere. Carbon dioxide exchange between the atmosphere and the surface waters of the ocean occurs through molecular diffusion. The diffusion is due to differences in CO_2 gas pressure between the atmosphere and oceans [Takahashi et al., 2002]. Carbon dioxide will enter the ocean when the CO_2 gas pressure of the atmosphere is higher than that of the ocean surface. The surface ocean currently absorbs approximately 30% of the CO_2 emitted to the atmosphere from human activities [Riebesell et al., 2010]. The amount of CO_2 that the ocean is absorbing is increasing due to the increase of atmospheric CO_2 concentration [Riebesell et al., 2010].

The capability of the global ocean to hold more CO_2 than the atmosphere is due to what happens when CO_2 reacts with the seawater.

Solution:

 $CO_2(atmospheric) \Leftrightarrow CO_2(dissolved)$

• Conversion to carbonic acid:

 $CO_2(dissolved) + H_2O \Leftrightarrow H_2CO_3$

• First ionization:

 $H_2CO_3 \Leftrightarrow H^+ + HCO_3^-$ (bicarbonate ion)

• Second ionization:

 $HCO_3^- \Leftrightarrow H^+ + CO_3^{2-}$ (carbonate ion)

 CO_2 dissolved in seawater reacts with the water to disassociate into several ions [Emerson & Hedge, 2008]. When CO_2 reacts with water it forms weak carbonic acid (H₂CO₃), which is then dissociated into bicarbonate and carbonate [Archer, 2010]. The interaction of these species in seawater creates a chemical buffer system, regulating the pH and the pCO₂ of the oceans. Most of the inorganic carbon in the ocean is in the form of bicarbonate (~88%), with the concentrations of carbonate ion (11%) and CO_2 (1%) making up the rest. This process increases the buffering capacity of the surface water and reduces the partial pressure of CO_2 in the water, thus allowing more diffusion from the atmosphere [Zeebe & Wolf-Gladrow, 2001]. This means that the ocean can hold large stores of carbon. Henry's Law describes the solubility of CO_2 ,

$$\left[CO_{2}\right] = K_{0}(T,S) \cdot fCO_{2}$$

$$[1.2]$$

where $[CO_2]$ is the concentration of CO_2 in surface waters, fCO_2 is the fugacity (approximately the partial pressure) of CO_2 in surface waters, and K_0 is the equilibrium constant as function of T and S.

If the surface ocean is in equilibrium with the atmosphere then the atmospheric pCO_2 is controlling the surface water pCO_2 . Therefore, if there is a change in the atmospheric pCO_2 then this will cause an imbalance in the atmospheric-oceanic equilibrium resulting in the ocean compensating by absorbing CO_2 leading to an increase in the oceanic pCO_2 . The temperature dependence of Henry's Law shows that colder waters store more CO_2 than warmer waters [Takahashi et al, 2002].

Figure 6 illustrates the exchange of CO_2 between the ocean and the atmosphere. The most significant amount of CO_2 uptake occurs in the North Atlantic. Since cold seawater holds more CO_2 , waters that are cooling (waters moving towards the poles) tend to take up carbon [Takahashi et al., 2002]. Conversely waters that are upwelling and warming tend to release carbon [Takahashi et al., 2002].



Figure 6: The mean annual air-sea flux for 2008. Green: saturated, no net gas exchange. Yellow/red: saturated, out-gassing. Blue: undersaturated, flux into the ocean [Source: Takahasi et al., 2009].

The net gas exchange is proportional to the concentration difference between air and water [Siegenthaler & Sarmiento, 1993]. In the tropics, where the water is warm, there is a larger amount of out gassing; while in the high latitudes the colder water temperatures lead to a greater flux of CO₂ into the ocean [Fletcher et al., 2007]. A complex pattern in the Southern Ocean exists, but overall the Southern Ocean is a sink of CO₂ [McNeil et al., 2007]. The net CO₂ gas exchange between the ocean and the atmosphere is described by the following set of equations [Siegenthaler & Sarmiento, 1993; Zeebe & Wolf-Gladrow, 2001],

$$F_{down} = A \cdot k_W \cdot K_0 \cdot pCO_{2,ATM} = A \cdot k_W \cdot \left[CO_{2,ATM}\right]$$
[1.3]

$$F_{up} = A \cdot k_W \cdot K_0 \cdot pCO_{2,OCEAN} = A \cdot k_W \cdot \left[CO_{2,OCEAN}\right]$$
[1.4]

$$F_{net} = A \cdot k_W \cdot K_0 \cdot \left(pCO_{2,ATM} - pCO_{2,OCEAN} \right)$$
[1.5]

$$F_{net} = A \cdot k_W \cdot K_0 \cdot \left(\left[CO_{2,ATM} \right] - \left[CO_{2,OCEAN} \right] \right)$$
[1.6]

where F_{net} is the atmosphere to ocean CO₂ flux (mol), *A* is the area (m²), K_0 is the solubility (following Henry's Law) in mmol m⁻³ µatm⁻¹, [CO₂] is the concentration in ml/l for standard conditions, and k_W is the gas exchange coefficient (m/yr) [Zeebe & Wolf-Gladrow, 2001].

Alkalinity, and pH

Total alkalinity is defined as the concentration difference between proton acceptors (H^{+}) and proton donors. It can be approximately understood from charge

balance. Seawater is electro neutral

$$[Na^{+}] + [K^{+}] + 2[Ca^{2+}] + \dots - [Cl^{-}] - [NO^{-}] - [HCO^{-}] - 2[CO^{2-}] - 2[CO^{2-}] = 0$$
[1.7]

More specifically, total alkalinity (TA) is a measure of the amount of proton acceptors above a reference level. The alkalinity of water is a measure of its acid-neutralizing capacity.

$$TA \approx \left[HCO_3^{-}\right] + 2\left[CO_3^{2-}\right]$$
[1.8]

For practical application total alkalinity can be approximated by its largest contributions, which are

$$TA \approx [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+]$$
 [1.9]

An uptake or release of CO_2 by the ocean does not cause a change in the total alkalinity. It will however, result in a change of pH (acidification of the ocean). For example, if the partial pressure of the system is increased then more CO_2 dissolves in water, pH will decrease and all of the concentrations of all components in total alkalinity expression change, but the total alkalinity stays constant. The alkalinity is only changed through interactions with biology and minerals, and by changes in salt concentration due to evaporation and precipitation.

The pH of seawater results from the chemical equilibrium of the different forms of dissolved inorganic carbon. When CO_2 reacts with water and dissociates it creates an excess of H⁺. Since pH is inversely proportional to the logarithm of H⁺ ions, an increase in H⁺ ions will lead to a decrease in pH.

$$pH = -\log_{10}\left(\left\lfloor H^{+}\right\rfloor\right)$$
[1.10]

The Biological and Physical Pumps

The solubility pump is a physical-chemical process that transports carbon in the form of dissolved inorganic carbon from the ocean's surface to the deep ocean. Two distinct processes in the ocean acting together drive the solubility pump. The first is the fact that the solubility of carbon dioxide is an inverse function of seawater temperature. The second process is the driving of the thermohaline circulation by the formation of cold and dense deep water at high latitudes. These two processes act together to pump carbon from the atmosphere into the depths of the ocean. Consequently, deep water contains a high concentration of dissolved carbon due to the fact that it has the same conditions as the surface water that absorbs high amounts of carbon.

One consequence of the inverse relationship between solubility on water

temperature is that when deep water upwells in warmer, equatorial latitudes, it outgasses carbon dioxide to the atmosphere. On the other hand, colder waters lead to a large flux of carbon dioxide into the ocean.

The ocean is also full of plant life that, in the presence of sunlight, uses CO_2 and nutrients in the seawater to create organic matter. Most of the carbon dioxide removed from seawater by biological processes is quickly recycled back to CO_2 by the ocean surface food web, while a small amount of the waste matter sinks down into the deep water [Sarmiento & Gruber, 2006].



Figure 7: The biological pump occurs due to the death and sinking of primary producers. 10% of the primary production makes it to the deep ocean, while only 1% is buried in the sediment [Source: Aluwihare, 2011].

The sinking of biological matter moves carbon from the surface of the ocean to the deep ocean, storing carbon away from the atmospheric reservoir. This is illustrated in Figure 7 and is known as the biological CO₂ pump [Archer, 2010]. The carbon that reaches the deep ocean is either organic carbon or particulate inorganic carbon in forms such as calcium carbonate. The organic carbon that reaches the deep ocean is mostly sinking particulate matter, however some is in the form of dissolved organic carbon. Although only about 10% of the primary production sinks to the deep ocean, it is still an important sink for carbon because it is a long-term sequestration of carbon away from the surface ocean.

Presently about one third of anthropogenic emissions are entering the ocean, but the biological pump does not play a significant role in this. This is mostly because the biological productivity is limited by light and nutrient availability. This leaves the potential to increase the carbon sequestration by increasing the biological pump through increasing the nutrient supply. An increase in the supply of silicon could lead to a significant increase in diatom growth and therefore the biological pump.

Additionally, climate change may have a negative impact on the biological pump. Warming of the ocean could lead to stratification of the surface ocean, reducing the nutrient supply and thus reducing primary production. Changes in the pH caused by ocean acidification may affect hard shell organisms leading to a reduction in the biological pump by altering the hard tissue pump. The drop in pH level may also negatively affect photosynthesizing organisms that are sensitive to pH levels. The decrease in primary production would lead to a decrease in the amount of carbon that is exported to the deep ocean.

The export production describes the amount of dead organic material produced by primary production that is not recycled and sinks to the sea floor [Ruddiman, 2001]. The sinking material is called detritus and is composed of mostly organic material. The efficiency of the oceans biological pump E_{BP} , and therefore the efficiency of carbon sequestration, depends on the ratio of export production to primary production (NPP)

e-ratio:
$$e = \frac{\text{export P}}{NPP}$$
 [1.11]

The e-ratio is important because it describes how effectively the biological pump sequesters carbon. When the supply of nutrients is limited then it will limit the growth of all phytoplankton and the export of particulate organic carbon (POC) from the surface ocean [Ridgwell & Archer, 2002].

Phytoplankton

Phytoplankton are a diverse group of organisms that utilize nutrients that are generally supplied from below through upwelling to perform primary production through photosynthesis [Ruddiman, 2001]. Oceanic chlorophyll containing plants (phytoplankton) utilize nutrients in the presence of light to perform photosynthesis:

$$CO_2 + H_2O \rightarrow O_2 + sugars$$
 [1.12]

In addition to light, phytoplankton require carbon, nitrogen, phosphorus and O_2 to perform photosynthesis. These nutrients are taken up in the following rough proportions:

Surface Stoichiometry: $C: N: P: O_2 = 106:16:1:-138$

Stoichiometry below 400m: $C: N: P: O_2 = 117: 16: 1: -170$

This relationship is called the Redfield ratio [Redfield et al., 1963]. Marine biological production is limited by the availability of N, P and Fe. In addition to these,

diatoms also require silicon for survival. When the photosynthesis reaction proceeds in the reverse order, it represents the respiration or combustion of that organic matter.

$$O_2 + sugars \rightarrow CO_2 + H_2O$$
 [1.13]

The phytoplankton are the primary producers and make up the base of the food chain [Ruddiman, 2001]. Zooplankton graze on the phytoplankton and the larger, higher order animals feed on the zooplankton and phytoplankton.

In the context of this research, phytoplankton can be separated into two main groups: siliceous phytoplankton, called diatoms, and non-siliceous phytoplankton. Diatoms differ from smaller groups of phytoplankton by: (1) si-limitation, (2) different grazing patterns, (3) different sinking properties [Bopp et al., 2005].

Diatoms, single celled algae with silica walls, are a major component of marine phytoplankton [Bopp et al, 2005]. Diatoms are relatively large group of phytoplankton that incorporate silicon in the form of silicic acid (Si(OH)₄), also called silicate or dissolved silica, for the growth and production of their siliceous frustules (cell well) in the form of opal. This results in low concentrations of silicic acid in surface waters [Sarmiento & Gruber, 2006].

Diatoms are the dominant group of phytoplankton when growth conditions are optimal. Globally diatoms contribute about 40% of the primary production, but in certain regions are responsible for up to 75% of the primary production in the ocean [Wells, 2003; Bernard et al., 2010]. Additionally, diatoms are very efficient exporters of fixed carbon to the deep ocean [Wells, 2003; Bernard et al., 2010]. When the nutrient supply runs out, the diatoms aggregate into flocks that sink quickly [Sarmiento & Gruber, 2006] and can account for about 40% of biological pump of CO_2 [Sarmiento & Gruber, 2006].

Anthropogenic Perturbation

While humans pump CO_2 into the atmosphere, natural processes are significantly damping the rate of accumulation of this carbon [Sarmiento & Gruber, 2002; Sabine et al., 2004]. Carbon dioxide is naturally removed from the atmosphere, but the natural removal processes cannot keep up with increasing anthropogenic input [Sarmiento & Gruber, 2002; Sabine et al., 2004; Griggs, 2002]. The oceans and land absorb most of this carbon, leaving about only 40% in the atmosphere to cause climate warming [Griggs, 2002]. Some suggest that a larger percentage of recent emissions have remained in the atmosphere than usual [Le Quéré et al., 2009]. This leads some to believe that the natural sinks for CO_2 are

becoming saturated.



Figure 8: Atmospheric CO₂ levels measured at Mauna Loa, Hawaii since 1958 [Source: NOAA].

The first accurate long-term measurements of carbon dioxide concentrations in the atmosphere were performed in 1958 [Keeling, 1958]. In Figure 8 the increasing trend in atmospheric CO_2 levels over the last half-century is easily observed. In order to acquire measurements before 1958, air trapped in ice cores from the Antarctic were used [Raynaud et al., 1993]. The amount of CO_2 in the atmosphere has risen to the current level of 390 ppm from about 280 ppm before the Industrial Revolution started in the mid-18th century [Archer, 2010]. This marks a 39% increase in the atmospheric CO_2 concentration [Archer, 2010]

There is an obvious long term trend of increasing atmospheric CO_2 due to anthropogenic activities. Researchers have come to the consensus that we are already experiencing an abnormal global warming effect due to these increased levels and that the effect will continue if nothing is done to stop it. As a result of the rising CO_2 levels, the global surface temperature has risen significantly. Figure 9 shows four independent, nearly identical records of the warming trends.



Figure 9: Four independent records of global surface temperatures [Source: Simmon].



Figure 10: Even if future emission rates are greatly reduced the atmospheric CO₂ level will continue to rise, with the CO₂ concentration eventually stabilizing at a level that is at least double that of preindustrial times [Source: IPCC, 2001].

Figure 10 shows the carbon concentration projections as reported by the IPCC (2001) and used as the basis for climate model projections in the Fourth Assessment Report. If economic and emission growth continues at the same rate as today then by 2100 we will be emitting about 30 PgC per year. Even if we take major steps to reduce emissions immediately, by 2100 we will have committed ourselves to 2°C warming above pre-industrial levels. If all anthropogenic carbon-dioxide-emitting activities were instantly stopped, carbon dioxide levels and temperatures would still continue to rise for a long time before peaking. Even if the rate of fossil fuel

emissions decreased rapidly in the next one hundred years, the atmospheric CO₂ concentration would stabilize at a level at least double that of pre-industrial times.

Effect of Increased Atmospheric CO₂ on Ocean Carbon Uptake

The ocean has taken up about 30% of the CO_2 released to the atmosphere by anthropogenic sources since pre-industrial times [Archer, 2010; Sabine et al, 2004]. Almost all of this CO_2 resides in the first kilometer of the surface of the ocean and has not penetrated any deeper due to slow ocean mixing times [Sabine et al, 2004].

More carbon is driven into the oceans by the solubility mechanism [Sabine et a., 2004], due to an anthropogenic increase in the atmospheric CO_2 concentration. The ocean is expected to eventually take up about 85% of the anthropogenic CO_2 , but this will happen over long timescales [Archer, 2010; Sabine et al, 2004; Gruber et al., 2009] due to the long time frames over which the surface water mixes with the deeper ocean waters. The ability of the ocean to absorb carbon decreases as the concentration of carbon increases. Eventually, the ocean will reach a level where it cannot absorb any more carbon [Archer, 2010; Sabine et al, 2004; Gruber et al., 2009].

Model estimations have shown that global warming leads to reduced rates of carbon uptake, with climate change affecting both the solubility pump (due to warming of surface waters) and the biological pump. There are many changes in ocean physics and circulation as a result of global warming such as the increase in oceanic temperature, increased oceanic vertical stratification, decreased convective overturning, and decreased arctic sea-ice cover [Bopp et al., 2005]. These changes lead to a reduction of the ability of the ocean to absorb carbon. Furthermore, surface warming leads to an increase in carbon outgassing to the atmosphere.

In addition there are biogeochemical feedbacks in response to climate variability. The increased stratification previously mentioned and nutrient-depleted conditions induced by climate change in the surface ocean favor small phytoplankton [Bopp et al., 2005]. This leads to diatoms being replaced by small phytoplankton resulting in a large decrease in oceanic primary production. Changes in the diatom distribution impacts oceanic carbon uptake by reducing the efficiency of the biological pump which leads to a reduction in the export ratio [Bopp et al., 2005].

Ocean Acidification

The ocean's uptake of carbon dioxide also leads to acidification. Ocean acidification is a result of carbon dioxide dissolving in water because when CO_2 is dissolved in seawater it leads to the formation of carbonic acid. The following

reactions lead to ocean acidification and are illustrated in Figure 11.

Reaction 1: First, atmospheric carbon dioxide combines with seawater to form carbonic acid.

Reaction 2: The carbonic acid then dissociated by losing hydrogen ions to form bicarbonate, lowering the pH of the water.

Reaction 3: The carbonate ions in the water combine with hydrogen and are no longer available for biological use.



Figure 11: Schematic showing the reactions that cause ocean acidification [Source: University of Maryland].

Since preindustrial times, the pH of the ocean has declined 0.1 pH units, from 8.2 to 8.1, meaning the ocean has become more acidic [Doney et al., 2009]. Assuming that the amount of carbon in the atmosphere continues to increase at the same rate then it will reach about 800 ppm by 2100 [The Royal Society, 2009]. Approximately one third of the excess atmospheric CO₂ will be absorbed by the ocean leading to a drop in pH levels from 8.1 to 7.8 (Fig. 12), resulting in increased ocean acidification [IPCC, 2007].

Ocean acidification will have some critically important consequences on marine ecosystems. The acidification of the ocean leads to negative impacts on many pH sensitive species [Doney et al., 2009]. It causes damage to coral reefs and places significant stress on species important to the marine food chain. Ocean acidification has an especially profound impact on all marine life that relies upon calcium carbonate to build shells and skeletons [Doney et al., 2009].



Figure 12: The change in surface seawater pH vs. time relative to the change in CO₂ and DIC concentrations for the last century and a half and for future predictions [Source: Zeebe & Wolf-Gladrow, 2001].

With declining pH, reef communities undergo fundamental changes such as a change in species richness and coral recruitment progressively decline with declining pH [Fabricius et al., 2011]. Reef development ceases at a pH of 7.7; therefore a pH below 7.8 is a catastrophic level and is the maximum tolerable threshold [Fabricius et al., 2011]. If carbon dioxide emissions continue to increase at the current rate, this pH threshold will be reached by the end of the century.

1.4 Natural Weathering and Geoengineering Involving Weathering

The silicon cycle differs from other elemental cycles, such as carbon, in that silicon does not have a gaseous phase. Additionally, the solubility of silicon compounds is limited and therefore most silicon is found in sedimentary or particulate form [Sarmiento & Gruber, 2006]. Formation and dissolution of silicate rocks occurs primarily through weathering and geochemical reactions

In order for silicon to be made available for biological activity, the silicate rocks must be broken down by either physical weathering (by wind or ice) or chemical weathering (reaction with acidic and oxidizing substances). Once silicon is made available, it is then cycled by biological activity [Sarmiento & Gruber, 2006].

Silicon in the Oceans

The products of the weathering are then transported from the land to the ocean via rivers or groundwater. The Earth's rivers are the most significant input of reactive silicic acid for the global ocean (Table 3).

		Global flux (10 ¹⁴ g/yr)
Sources	Rivers	1.57
	Air-born	0.14
	Seafloor erosion	0.11
	Hydrothermal circulation input	0.05
	Total	1.87
Sinks	Coastal deposition of biogenic silica	0.16
	Oceanic deposition of biogenic silica	1.72
	Total	1.88

Table 3: Global silicic acid sources and sinks [Source: Laruelle et al., 2009; Nelson et al., 1995].

Once in the oceans, the dissolved silica input is taken up by biological activity to form biogenic silica [Bernard et al., 2010]. Dissolved silica (silicic acid, or H₄SiO₄) as with other nutrients is often absent from surface waters because it is used by phytoplankton [Conkright et al., 1994]. The difference between silicon and other limiting nutrients, such as phosphate or nitrate, is that silicic acid is vital only for diatoms, while an insufficient supply of any of the other nutrients restricts virtually all phytoplankton growth [Ridgwell & Archer, 2002; Nelson et al., 1995]. By restricting the growth of phytoplankton, the export of particulate organic carbon (POC) from the surface ocean is also restricted [Ridgwell & Archer, 2002]. After the diatoms die, they cluster and begin to sink towards the seafloor. As the frustules sink towards the seafloor some is remineralized, making it once again biologically available. A portion of the dead organic material reaches the seafloor where it is buried and contributes to the pool of dead organic material called detritus. Detritus is then decomposed and dissolved, which releases the nutrients for possible uptake. The nutrients are then eventually returned to the ocean surface via upwelling [Ridgwell & Archer, 2002].

There is a close coupling of the biogeochemical cycles of carbon (C) and silicon (Si) [Lerman & MacKenszie, 2010], which causes silicon to have a large effect on the efficiency of the biological carbon pump. This close relationship is due to the major role that diatoms play in the biological pump of CO₂ and to the presence of silica-rich sediments in areas that play a major role in air–sea CO₂ exchange [Ragueneau et al., 2000]. Diatoms are different from other phytoplankton in that they require Si, in the form of silicic acid (Si(OH)₄) for growth and utilize this silicic acid for the production of their frustules (made of biogenic silica, bSiO₂) [Ragueneau et al., 2006]. Diatoms (Fig. 13) employ a unique strategy to protect their frustules from

rapidly dissolving away in seawater that is understaurated in silicic acid. This unique strategy results in an intimate interaction between C and Si [Ragueneau et al., 2006].



Figure 13: Pictures of several species of diatoms, which are silicon based phytoplankton. When enough silicate is present diatoms will outcompete other species of phytoplankton [Source: Zanette].

If light and nutrient conditions are favorable for growth and silicic acid is present then diatoms out-compete most other phytoplankton species and dominate the ecosystem [Aksnes et al., 1994; Egge, 1998; Egge & Aksnes, 1992]. On the other hand, if the availability of silicic acid is limited, diatoms will play a less important role. Diatoms are responsible for the production of biogenic silica, but do not produce any calcium carbonate. The production of calcium carbonate (CaCO₃) is left to the nonsiliceous phytoplankton [Ridgwell & Archer, 2002]. Therefore changes in the amount of silica, which benefits diatoms, may then affect the ratio of CaCO₃ to POC exported from the surface layer of the ocean [Ragueneau et al., 2000]. These changes would then lead to changes in the ocean chemistry and changes in the atmospheric mixing ratio of CO_2 (pCO₂) [Ridgwell & Archer, 2002].

Olivine is a magnesium iron silicate with a composition close to $(Mg,Fe)_2SiO_4$ (Fig. 14). The iron and magnesium can be substituted for each other readily within the crystalline structure. It is one of the most common minerals on Earth and can be found in ultramafic igneous rocks. Some ultramafic rocks, called dunite, can be composed almost entirely of olivine. The Earth's mantle is dominated by olivine and huge amounts of olivine rocks are exposed at the surface of the Earth [Schuling & Krijgsman, 2006].



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Figure 14: Olivine is one of the most common minerals and can be found on every continent [Source: Weller].
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Natural weathering and the subsequent precipitation of Ca and Mg carbonates are the main mechanisms that work to remove carbon dioxide from atmosphere [Schuling & Krijgsman, 2006]. On Earth, running water, wind, and ice act to continually remove weathered rock [Schuling & Krijgsman, 2006]. This exposes fresh rock, which can then be weathered, depleting the Earth's atmosphere of CO₂ following the general reaction [Schuling & Krijgsman, 2006]:

fresh silicate rock + $H_2O + CO_2 \rightarrow soil + cations + HCO_3^{-1}$ [1.14] The calcium and magnesium released during weathering combine in the oceans with the carbonate to form limestone and dolomite, which are the major sink for CO₂. The second major sink for CO₂ is the organic matter that sinks into the sediments.

This reaction proceeds naturally and requires no excess energy. It is in fact an exothermic reaction, releasing a small amount of heat.

The long-term mechanism that stabilizes the Earth's climate is called the weathering CO_2 thermostat [Archer, 2010]. Figure 15 illustrates how this mechanism stabilizes Earth's climate by regulating CO_2 concentration in the atmosphere, which in turn regulates temperature. As the temperature of the planet increases, it accelerates the hydrologic cycle, which causes more weathering and more CO_2 uptake. As the temperature of the Earth decreases the opposite happens, the hydrologic cycle slows down and so does the amount of weathering.

Unfortunately, this stabilizing force happens on geological timescales, on the order of hundreds of thousands of years [Archer, 2010]. Since natural weathering is the process that controls the CO_2 concentration in the atmosphere, it seems logical to use weathering as a tool to reduce rising CO_2 levels [Schuling & Krijgsman, 2006]. If the weathering process is enhanced, huge amounts of CO_2 sequestration can be achieved.



Figure 15: Flow chart depicting the Earth's naturally occurring weathering thermostat [Source: Stott].

Geoengineering with silicates

Carbon sequestration via mineral weathering was first mentioned by Seifritz in his 1990 paper. Mineral sequestration, as defined by Goldberg et al. (2001), involves the reaction of CO₂ with minerals to form geologically stable carbonates. The artificially enhanced weathering of olivine is one option for enhancing the ocean carbon sink and providing sustainable sequestration of CO₂ [Laruelle et al., 2009]. Precipitation on the continents drives the natural weathering of rocks and the transport of silica to the ocean [Laruelle et al., 2009]. The natural weathering of silicate and carbonate minerals is a huge natural sink for carbon and sequesters about 0.5 PgC per year [Matter & Kelemen, 2009; Zaihua et al., 2011]. Artificial enhancement of geological carbon absorbing processes would increase the annual sink for carbon. According to Schuiling, this method is the most feasible way to reduce the CO₂ content of the atmosphere and counteract the ocean acidification [Schuiling & Krijgsmand, 2006].

There are some distinct advantages that motivate the need for further research on the sequestration of CO_2 with silicates. The first is the abundance of the materials [Herzog, 2002]. As said earlier, olivine is one of the most common minerals on earth and silicon is one of the most common elements in the Earth's crust, second only to oxygen [Huijgen & Comans, 2003]. The second advantage of carbon sequestration via olivine is that it sequesters carbon on long time-scales [Huijgen et al., 2005]. Other proposed options for carbon sequestration have the possibility of "leakage" that will quickly return CO_2 to the atmosphere [Herzog, 2002]. Olivine is well studied and has known dissolution kinetics [Köhler et al., 2010]. Olivine
dissolves readily when in contact with CO₂ and water according to [Huijgen et al., 2005]:

$$Mg_2SiO_4 + 4CO2 + 4H_2O \rightarrow 2Mg^{2+} + 4HCO_3^- + H_4SiO_4$$
 [1.15]

The reaction products of olivine dissolution are silicic acid, magnesium ions and bicarbonate. Olivine dissolution is a CO_2 neutralizing reaction that sequesters a maximum of 4 moles of CO_2 per mole of olivine [Köhler et al., 2010]. Schuiling puts it in a more practical way saying 140 grams of olivine will sequester 176 grams of CO_2 [Schuiling & Krijgsmand, 2006]. The CO_2 consumed during these weathering reactions is of atmospheric origin. However, as Köhler et al. (2010) believe that this ratio of sequestration is somewhat optimistic. The actual amount of CO_2 sequestered will vary based on the initial state of the marine carbonate system. Although the efficiency is reduced due to the chemistry of CO_2 in seawater, this weathering process still provides an important atmospheric CO_2 sink [Gupta et al., 2005].

The rate of olivine weathering is largely dependent on the surface area of the grains of olivine. Olivine weathering depends on grain size and weather conditions, but the olivine weathering reaction can be sped up by grinding olivine to increase the surface area so that it weathers completely in a few years [Schuiling & Krijgsmand, 2006].



Figure 16: The weathering time of olivine varies greatly with grain size. The y-axis describes the percent of olivine that has weathered while the x-axis shows the amount of time that has passed in years [Source: Hangx & Spiers, 2009].

With a grain size of $\sim 10 \mu m$, under favorable conditions, the weathering reaction will take on the order of a couple years [Hangx & Spiers, 2009]. The amount of olivine dissolution is a function of time and grain size. In Figure 16 the left axis

shows the amount of olivine reacted while the right axis shows the amount of CO₂ sequestered per ton of olivine [Hangx & Spiers, 2009]. The sequestration of carbon through olivine weathering provides additional benefits, counteracting the ongoing acidification of the ocean [The Royal Society, 2009; Köhler et al., 2010; Brumfiel, 2009; Stephens & Keith, 2008]. The dissolution of olivine causes an increase in the total alkalinity (TA) of seawater by 4 units per mole of olivine dissolved [Köhler et al., 2010]. The total alkalinity of the ocean has a large influence on the solubility of carbon dioxide in seawater. According to Kheshgi (1995) increasing the total alkalinity by one mole increases the carbon content of the ocean by 0.89 moles.

Additionally, the primary production in the ocean will increase, which will lead to an increased amount of export. This increase in the biological pump will lead to an increase in the amount of carbon sequestration.

In theory this sequestration method will have relatively few ecological consequences because we are simply simulating a natural process [The Royal Society, 2009]. Olivine weathering output is low in deleterious elements. Nickel is the most abundant potential contaminant in olivine-rich rocks, but is present in trace amounts [Schuiling & Krijgsman, 2006].

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Chapter 2: Model and Methods

2.1 Introduction

The goal of this research is to investigate the value and impact of artificial weathering as a possible carbon capture method. Numerical modeling provides the best method to obtain the results for analysis. The modeling is performed using a coupled physical-biogeochemical model, where the complete physics of the ocean is coupled to a reduced-complexity biological model [Stow et al, 2009]. The model to be used in the study, a global setup of the state-of-the-art ocean general circulation, the MITgcm circulation model, coupled to coupled to the REcoM-2 pelagic ecosystem model, which distinguishes between diatoms and non-diatoms [Hohn, 2008] has been chosen. Some changes and extensions were made to the model specific to this study. Using the updated model configuration we were able to focus on scenario development, implementation, and performing simulations. The data was then exported to MATLAB for analysis.

2.2 The Biogeochemical Model

The complexity of biological processes in the ocean present huge problems in modeling, therefore the models used are of a reduced complexity [Stow et al., 2009]. The ecosystem model, called REcoM-2 (Regulated Ecosystem Model), is the second iteration of the REcoM model that is based on the physiological model for phytoplankton adaptation to light, nutrients, and temperature by Geider et al. (1998) [Schartau et al., 2007]. The first iteration of the REcoM model is an ecosystem model that describes the cycle of nitrogen and carbon and possesses individual equations for phytoplankton chlorophyll dynamics. The basic model kernel explicitly decouples carbon from nitrogen fluxes with most parameterizations for phytoplankton growth being adopted from Geider et al. (1998). Mass fluxes within the ecosystem are primarily regulated by the carbon-to-nitrogen (C:N) utilization ratio of phytoplankton. The REcoM-2 model is a full biogeochemical model that describes the physiological adaptation of phytoplankton, the response to changing conditions and the cycling of several nutrients (C, N, Si, Fe), including processes such as the mortality of phytoplankton from zooplankton grazing and the formation of detritus amongst other processes [Schartau et al., 2007]. The REcoM-2 model has been extended to include a regulatory model of diatom physiology that includes limitations by Si and Fe availability and accounts for diatom blooms, opal export, and iron explicitly [Hohn,

2008; Schartau et al. 2007; Losch et al., 2008]. The Hohn (2008) version of the REcoM model added four additional state variables: dissolved silicate, dissolved iron, and a biogenic silicate compound in phytoplankton and detritus. We added additional state variables for phytoplankton and detritus calcium carbonate, bringing the total to twenty-one state variables. The initial conditions for the 21 state variables of REcoM are estimated from observations and tuning experiments. Figure 17 is a flow chart illustration of the REcoM-2 model.



Figure 17: The REcoM schematic diagram shows the compartments and inter-compartmental flows of the upper mixed layer ecosystem.

Each of the twenty-one state variables has a corresponding partial differential equation that determines the dynamical evolution of the various components of the model: dissolved nutrients, two phytoplankton classes (Phy and Dia), zooplankton (Zoo), alkalinity, and detritus (Det) in the different currencies: N, C, Si, and Fe [Fennel, 2001]. The two phytoplankton classes are diatoms, which are the larger silicon dependent phytoplankton, and all other non-diatom phytoplankton species.

Most parameters were already tuned, but since state variables for calcium carbonate were added, it was necessary to tune this. This was done by tuning the fraction of organic to inorganic carbon production in phytoplankton. This has a classical value of 1/10 and describes the fraction of small phytoplankton cells that are calcifiers. To test if the value was valid for this model the average global CaCO₃ export over a five-year period was calculated to be $0.505 \text{ PgC} \cdot \text{yr}^{-1}$. The accepted global export value at 100 meters is $0.52 \pm 0.15 \text{ PgC} \cdot \text{yr}^{-1}$ [Dunne et al., 2007].

It was also necessary to tune the silicate parameter. The average global silicate export for the five-year control period was 102×10^{12} mol· yr⁻¹. The accepted global silicate export value at 100 meters is $101 \times 10^{12} \pm 35$ mol· yr⁻¹ [Dunne et al., 2007].

2.3 The Physical Model

The simulation of the ocean circulation is done using the MITgcm (Massachusetts Institute of Technology General Circulation Model) [MITgcm Group, 2002]. The MITgcm is a general circulation model, which we are using to model the ocean and sea ice. These are the most complex climate type of models available and are the best tools to provide detailed predictions of the future climate [MITgcm Group, 2002]. A detailed description of the model used in this research can be found in *MIT Climate Modeling Initiative* (2004) [Adcroft et al., 2004].

The MITgcm is numerical model that is useful in studying both oceanic and/or atmospheric conditions for both small and large-scale processes due to its nonhydrostatic capabilities. The MITgcm model can be applied to parameter and state estimation problems and can resolve many different processes. The MITgcm solves the time-dependent, Boussinesq-approximated Navier-Stokes equations and conservation equations for salinity and energy (in the form of an equation for potential temperature) [Losch et al, 2008]. As said earlier the model has nonhydrostatic capabilities allowing for the Navier-Stokes equations to be solved with or without the hydrostatic approximation.

The MITgcm model has been chosen because it is known to operate efficiently on multi-processor systems over a large range of processor numbers and computer architectures [Losch et al., 2008]. More information and the source code for MITgcm can be found at <u>http://mitgcm.org/</u> [MITgcm Group, 2002].

Model Grid

The model grid is a system used to represent and compute physical quantities, such as velocity and mass related quantities. The values at the grid points are used to solve the equations that govern the model. We are limited on the number of grid points because too many points would require laborious computational power, while too few point may lead to inaccurate representation of the physical processes of the ocean. While we try to use the highest number of grid points, this number is limited by computational capabilities. This limitation leads to some important ocean

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processes occurring on scales smaller than the model resolution.



Figure 18: Depiciton of the horizontal model grid used in the MITgcm. This is the well-known Arakawa C grid. It is a staggered grid that separates the eveluation of vector quantities and components [Source: IMCS]

The grid is a group of points representing the ocean i.e. the water is subdivided into 2-dimensional boxes. The grid has 2° resolution in the longitudinal direction. In the latitudinal direction there is $1/2^{\circ}$ resolution at the equator, 2° resolution in the Northern Hemisphere and the resolution scales with the cosine of the latitude in the Southern Hemisphere (i.e. at 60° the resolution is $2^{\circ} \times \cos(60^{\circ}) = 1.9^{\circ}$) with the Antarctic having a resolution between $1/2^{\circ} - 1/3^{\circ}$. In the horizontal, the arrangement of variables is as shown in Figure 18. This is the wellknown Arakawa C grid (Fig. 18) which is suitable for problems with fine horizontal resolution [Arakawa & Lamb, 1977]. The staggered Arakawa C-grid separates the evaluation of vector quantities, for example instead of evaluating both the east-west (u) and north-south (v) velocity components at the grid center, the westward velocity is defined on the westward side of the box, and the northward velocity on the northward side. The equations are discretized on a C-grid with η , H, and other scalar quantities defined in the center of a box, and the velocities u and v defined on the sides. The horizontal grid is separated into 180 cells in the east-west direction and 126 cells in the north-south direction. Just as a staggered grid is used in the horizontal, a staggered grid is also used in the vertical. The vertical grid consists of 30 grid cells of varying size with the lowest boundary of the bottom grid cell being at 5700 meters depth.

The staggering of the grid is due to the fact that the variables need to be located in suitable positions so that the resulting scheme yields maximum stability in calculation [Arakawa & Lamb, 1977]. The C grid is efficient at calculating the horizontal pressure gradients in the momentum equations and the flux divergences in both the momentum and continuity equations to a high numerical accuracy. The main weakness of the C grid is that the horizontal staggering components of the velocity vector causes difficulties in calculating the Coriolis terms due to the fact that we must average some quantities [Marshall et al., 1997; Arakawa & Lamb, 1977].

Ocean

The oceanic model is based on the Boussinesq approximation and because of this it conserves volume rather than mass [Stammer et al., 2003; Olson, 2006]. The upper surface of the ocean is a free surface, which is driven by the divergence of volume flux (Boussinesq) in the interior and the precipitation minus the evaporation [Olson, 2006]. The MITgcm ocean model uses velocities, temperature and salinity as prognostic variables and tracers in the ocean [Adcroft et al., 2004a]. The nonhydrostatic, incompressible Boussinesq equations used the model can be expressed as [Olson, 2006]:

$$\rho_0 D_t \vec{v} + 2\Omega \times \rho_0 \vec{v} + g\rho \vec{k} + \nabla p = \vec{F}$$
[2.1]

$$\rho_0 \nabla \cdot \vec{v} = 0 \tag{2.2}$$

$$\partial_t \eta + \nabla \cdot (H + \eta) \vec{v}_h = P - E$$
[2.3]

$$D_t \theta = Q_\theta$$
 [2.4]

$$D_t s = Q_s$$
 [2.5]

$$\rho = \rho(s,\theta,p) \tag{2.6}$$

where \vec{v} is the velocity vector in three-dimensions, p is pressure, ρ is the density, ρ_0 is a constant reference density, η is the sea-surface height, θ is potential temperature, s is salinity, g is the gravitational acceleration, H is the bottom depth, and \vec{F} , P - E, Q_{θ} , and Q_s are forcing fields [Olson, 2006].

Sea Ice

According to Adcroft et al. (2004b), the MITgcm sea ice model is a global model based on a variant of the viscous-plastic dynamic-thermodynamic sea ice model first introduced by Hibler in 1979. The sea ice model requires input from: winds, air temperature and specific humidity, downward longwave and shortwave radiations, precipitation, evaporation, and river and glacier runoff [Adcroft et al., 2004b]. While its output fields are surface wind stress, evaporation minus precipitation minus runoff, net surface heat flux, and net shortwave flux. In the regions of the ocean that are ice-free, bulk formulae are used to estimate oceanic

forcing from the atmospheric fields [Adcroft et al., 2004b].

Coupling

The variables between the ocean and sea-ice components are coupled every ocean time step. Both heat and water are conserved in the MITgcm coupling scheme.

2.4 Model Initialization and Spin-Up

In order to start a model run, the starting values for certain variables need to be specified. These include temperature, salinity, density, sea level, and velocity.

Surface Forcing

Results from a data analysis system are used to initialize the model. It is very difficult to use observations directly since they are so irregularly spaced and extensive error checking needs to be done. Climatological observation data from the World Ocean Atlas [Conkright et al., 1994] was used to initialize the model values of temperature and salinity from databases.

For the physics surface forcing fields (air temperature, wind speeds, humidity, short-wave radiation flux etc.) the CORE.2 data set [Griffies et al., 2008] is used. The CORE.2 forcing data (Coordinated Ocean-Ice Reference Experiments) [Griffies et al, 2008] was proposed by the CLIVAR Working Group on Ocean Model Development. The air-sea fluxes of momentum, heat, freshwater, and their components have been computed globally based on NCEP (National Centers for Environmental Prediction) data reanalysis from 1949 through 2006 [Large & Yeager, 2008]. The ocean is forced by the fluxes of freshwater, F, heat, Q, and momentum, τ .

$$\vec{\tau} = f_o \vec{\tau}_{as} + (1 - f_o) \vec{\tau}_{io}$$
[2.7]

$$F = f_o F_{as} + (1 - f_o) F_{io} + R$$
[2.8]

$$Q = f_o Q_{as} + (1 - f_o) Q_{io}$$
[2.9]

where R is the river runoff, which is based on observed estimates of precipitation and evaporation over the continents. A fraction of ocean surface is covered by seaice, leaving a fraction f_o exposed to the atmosphere. The subscripts "as" and "io" denote air-sea and ice-ocean fluxes respectively.

Spin-Up

Spin-up is the time taken for an ocean model to reach a state of statistical equilibrium under the applied forcing. It is difficult for global circulation models like

Chapter 2: Model and Methods

MITgcm to reach this state of equilibrium. While the upper ocean requires only 50 or so years to reach equilibrium, the deep ocean requires hundreds of years to adjust. To allow the deep ocean to reach equilibrium, it would be time consuming and the end state may deviate from observations.

The ocean model is initialized using data from the current ocean state (climatologies) and then is integrated forward in time, geostrophically adjusting to its initial state, until the model reaches some sort of stable state. Instead of running the model for hundreds of years, it is run until we are confident that model drift is not masking the variability that is actually due to changes in the surface forcing. The aim is to keep the model as close as possible to the data observations. Therefore a long spin-up where the model drifts far away from the initial state is not really desirable. Nevertheless, it is important to have at least a short spin-up phase so that it is possible to be sure that a change in the model is due to a change in the system and not to a model drift. In order to achieve at least a geostrophically adjusted circulation, but at the same time prevent too much model drift from realistic conditions, a spin-up time of 5 years was used for the model runs. One 5-year spin-up phile.

The equatorial band takes a few years to reach equilibrium, while the mid latitudes take longer (on the order of a decade) to reach equilibrium due to the fact that long Rossby waves travel slower at higher latitudes. A spin-up time of only a few days is required for wind driven flows, including Ekman pumping, to reach equilibrium. Therefore, the 5-year spin-up time will be sufficient for wind driven flows and the equatorial band to reach equilibrium.

2.5 Methods for Experimental Data Runs

The input of olivine was simulated via a flux of silicate and a separate flux of alkalinity. The silicate input flux has units of mmoles per square meter per second. The flux of alkalinity has the units of alkalinity per square meter per second.

Using the molecular weight of olivine (Mg₂SiO₄) as 153.31 grams, one petagram of olivine is thus equivalent to 6.5227×10^{12} moles. One mole of olivine contains one mole of silicate thus one petagram of olivine contains 6.5227×10^{12} moles of silicate. This then needs to be calculated as a flux:

$$Si_{input} = \frac{Si_{total}}{T * A_{ocean}} = 5.95671 \times 10^{-10} \left[\frac{\text{molSi}}{\text{s} \cdot \text{m}^2} \right]$$
 [2.10]

Where Si_{total} is the total olivine distribution per year in moles, T is one model

year and A_{ocean} is the area of the ocean in the model. In the model one year is equivalent to 360 days, which is 31,104,000 seconds. The total area of the ocean used in the model is 3.5205×10^{14} m².

In the model, the tracers are distributed once every second. In order to calculate the distribution of one petagram of olivine per year we must then divide through. Dividing through to get mmol would give the value used in the model for the average distribution of silicate per meter squared per second over the entire ocean for the input of one petagram of olivine. For different distribution scenarios the amount of olivine that each square meter receives would vary based on a weighting value. For example, in the river distribution scenario the grid cells associated with the Amazon River runoff would receive a higher weighting and therefore a higher percentage of the total silicate.

One mole of silicate is equivalent to an input of four units of alkalinity.

$$Alk_{total} = Si_{total} *4$$
[2.11]

This is due to the fact that olivine reaction results in the addition of four bicarbonate ions.

2.6 Distribution Scenario Description

The model was first run for a five-year control period in order to validate the accuracy of the model and to generate a baseline (Exp1).

Three different distribution scenarios were investigated: even distribution over the ocean, distribution depending on river runoff, and distribution based on shipping paths. Each distribution scenario was then tested with varying amounts of olivine input: one petagram, two petagrams, five petagrams, and ten petagrams of olivine. These scenarios and their identifiers are shown in Table 4.

The dissolution of one mole of olivine would, at the theoretical upper limit, sequestrate four moles of carbon dioxide. This is equivalent to one gram of olivine sequestering about 1.25 grams of CO_2 or 0.32 grams of carbon.

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Figure 19: The amount of CO₂ sequestered per amount of olivine.

Figure 19 shows the theoretical amount of carbon dioxide sequestered per amount of olivine input.

Distribution Scenario	Olivine Input (Petagrams)				
	None	1	2	5	10
Control Run	Exp1	-	-	-	-
Even Open Ocean Distribution	-	Exp2.1	Exp2.2	Exp2.3	Exp2.4
River Distribution	-	Exp3.1	Exp3.2	Exp3.3	Exp3.4
Ship Distribution	-	Exp4.1	Exp4.2	Exp4.3	Exp4.4
Even Open Ocean Distribution with No Alkalinity Flux	-	Exp5.1	Exp5.2	Exp5.3	Exp5.4
Even Open Ocean Long Term Run (40 Years)	-	-	-	Exp6	-

 Table 4: Identifiers for the olivine distribution scenarios.

Olivine input leads to an increase in the alkalinity and silicate fluxes into the ocean. Each second, an additional silicon and alkalinity flux is added to the surface ocean due to olivine dissolution. The major sources of dissolved silica to the marine environment contribute a natural input of approximately 0.2 Pg SiO₂ yr⁻¹ [Laruelle et al., 2009; Nelson et al., 1995; Treguer et al., 1995]. The amount of flux of silicate and alkalinity scales linearly with the olivine input. An input of 1 Pg olivine leads to a flux of about 3.62×10^{14} grams of silicate, which is double the natural flux. Additionally olivine input will lead to a varying increase in DIC due to an increase in the ocean's

alkalinity.

The short-term reaction of the system was investigated, with all runs done for a five-year period. All data from scenario runs was analyzed by comparing it to the control run.

Even Distribution over the Open Ocean (Exp2)

I then extend the research performed by Köhler et al. (2010) to the open ocean. The first scenario investigated was the distribution of olivine evenly over the open ocean. This scenario will later be referred to as Experiment 2 (Exp2) for clarification in the figures presented.

This distribution scenario has olivine being distributed across the entire ocean once every second at the rates shown in Table 4. This is not a very realistic scenario, as it would require constant olivine distribution over a huge area, but it is useful in illustrating the possible maximum effects of olivine distribution.

Distribution in the Rivers (Exp3)

The second distribution scenario followed the basic idea of Köhler et al. (2010) with distribution into the Earth's rivers (Exp3).

As the model calculates fluxes variables only for the oceans the silicate flux cannot be put directly into the rivers, but only in the places where the rivers enter the ocean (river mouths). To do this a silicate input file was generated using the river runoff taken from the CORE.2 data set [Griffies et al, 2008].

The silicate was distributed at river mouths and along coastlines in proportion to the percentage of river runoff that occurs at each grid cell relative to the total river runoff across the Earth with the majority of the river runoff in the world coming from the Amazon River.

To calculate the olivine flux distribution for the riverine input scenario the total amount of Si going into the world's in mmol/year was then divided by 31104000 seconds (1 year = 360 days) to calculate the total flux of Silicate in Si_{total} (mmol/sec).

$$Si_{total} = \frac{6.5227 \times 10^{15} [\text{mmolSi}]}{31104000 [\text{s}]} = 2.09706 \times 10^8 \left[\frac{\text{mmolSi}}{\text{s}}\right]$$
[2.12]

Then the river input F(x,y,t), which has units of $m^3/m^2/sec$. To get the total flux $F(t)_{total}$ form the integral over space, i.e. sum over all surface are boxes, multiplied by the area of the respective boxes A(x,y).

$$F(t)_{total} = \Sigma (F(x, y, t) * A(x, y))$$
[2.13]

where the Area of the land boxes has been set to zero by multiplying with the land

mask. $F(t)_{total}$ will then have the unit m³/sec⁻¹. Then the fractional water flux W(x,y,t) can be formed by

$$W(x,y,t) = \frac{F(x,y,t)}{F(t)_{total}}$$
[2.14]

W(x,y,t) will then the unit m⁻². Finally, the Si flux (Si(x,y,t)) file is constructed by multiplication of W(x,y,t) with the total Si flux (Si_{total})

$$Si(x,y,t) = Si_{total} * W(x,y,t)$$
[2.15]

Distribution over Shipping Paths via Ships of Opportunity (Exp4)

The third possible distribution scenario is distribution of ground olivine via ballast water of ships of opportunity (Exp4). Currently "Ships of Opportunity" are being used for data collection. These are commercial ships that have been equipped with scientific equipment to monitor water conditions. These volunteer merchant ships routinely transit strategic shipping routes. The ballast water of volunteer commercial and merchant ships could be fertilized with ground olivine and discharged over the entire shipping route.

The NOAA COARDS (Cooperative Ocean/Atmosphere Research Data Service) data set is used to serve as a proxy for shipping paths. The COARDS data set is a record of the number of sea surface temperature readings taken per month by ships over the ocean. The data set contains information on how many measurements were taken in a particular grid cell from the year 1959-1997. While this temperature measurement frequency distribution is not the actual ship track distribution, it can serve as a proxy for ship tracks across the ocean.

Notice that the distribution is heavily biased towards the Northern Hemisphere. The Southern Hemisphere, especially the Southern ocean has very little ship activity. This is significant because the large, cold water Southern Ocean could possibly play a large role in carbon sequestration, but in this scenario would be left mostly untouched with very little to no olivine distribution. Figure 20 shows the number of months with a measurement, but it is also possible to have a more detailed view with the number of measurements per day.

Using the sea surface temperature measurement file as a proxy, a shipping "density" file was constructed. This file was interpolated onto the model grid and normalized so that the area of the integral of ship densities was equal to one. The density of shipping routes has the unit $1/m^2$. To convert this to a silica-flux file it was only necessary to multiply the density field with the desired total flux (in mmol/sec) to obtain the matrix for the silica flux per square meter.

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Figure 20: Record of sea surface temperature measurements taken via ships. This distribution can serve as a proxy for shipping tracks.

Two Additional Experimental Data Runs (Exp5 and Exp6)

In addition to the three scenario runs described above, two additional runs were performed. The first (Exp5) is the same scenario as the even open ocean distribution (Exp2) with only silica input. Alkalinity input was excluded in order to obtain an understanding of the two different mechanisms acting to sequester carbon; the changes in ocean chemistry due to alkalinity input and the increased biological pump due to silicon input.

There may be other long-term effects that are only visible after more time. After all we are interested in the potential of this method as an effective way to counteract the negative effects of global warming over the long term. In order to obtain a basic idea about the long-term effectiveness of this method, one model run was done with even distribution of olivine over the open ocean for a period of 40 years (Exp6).

Chapter 3: Results

3.1 Control Run (Exp1) and Model Validation

The model was first run for a five-year period with no additional silica or alkalinity inputs in order to validate the model parameters. Data obtained by NASA's Sea-viewing Field of view Sensor (SeaWiFS) provided the means to validate the model's surface distribution of chlorophyll at the global scale [Bopp et al., 2005]. The chlorophyll data for validation comes from the merging of the output from 3 satellite instruments (SeaWiFS, MERIS and MODIS), provided by the globcolor project (<u>www.globcolor.info</u>). The method to merge the data follows Maritorena and Siegel (2005). Additional data from other sources provided the means to further validate the model parameters. The validation data was constructed through a combination of satellite data, measured data and interpolation.

The carbon export production value was taken as the weighted average between the export at grid box number 6 (87.5 meters) and box number 7 (115 meters) in the vertical grid, which is equivalent to 100 meters depth. On average over the five-year control period, the net primary production is 29 PgC per year while the total carbon export at 100 meters is 8.92 PgC per year. A large spread in primary production (PPI) values is found for both satellite color algorithms (35 to 68 PgC yr⁻¹) and GCMs (37 to 78 PgC yr⁻¹) [Schneider et al., 2008]. Export fluxes of organic carbon are more difficult to measure directly and have to be referred to a certain depth level, which is not done the same throughout all studies. Estimates from Schneider et al. (2008) suggest that global carbon export is in the range of 5 to 11 PgC yr⁻¹ at 100m. Both the global primary production and global carbon export production are a bit underrepresented in my model setup. Nevertheless, the patterns of spatial and temporal variability are similar between the model used and other approaches. The distribution patterns are well represented by the model with high values of primary production along the equator and in upwelling zones.

The export production values of 8.92 PgC yr⁻¹ with a primary production of 29 PgC yr⁻¹ results in a biological pump efficiency (e-ratio) of 30.70%. The efficiency of the biological pump is overestimated in the model, with the actual measured value for efficiency being closer to 20%. The efficiency of the biological pump is higher for this model than measured values because the primary production is under-represented in the model.

Seasonal variations in primary production and export production both show

significant variation over the course of the year (Fig. 21). The zonal integral of primary production (Fig. 21) shows a prominent maximum in the equatorial region.



Figure 21: All figures are for the final year of Exp1. Top-left: The total NPP over the entire ocean. There is an obvious seasonal variation. Top-right: The total export at 87.5 meters summed over the entire ocean, with an observable seasonal variation in export. Bottom-left: Zonal integral of net primary production over latitudinal circles in Pc C yr⁻¹ deg⁻¹. In the model there is a significant peak across the equator in primary production. This is a bit over-represented in the model in comparison to satellite-estimated primary production. Bottom-right: The export depth profile shows export increasing in the photic zone and dropping off exponentially once exiting the photic zone.

The model is relatively coarsely resolved (on the order of 100-200 km spatial resolution in the horizontal) and is unable to represent the action of the energetic mesoscale eddy field that has length scales on the order of the Rossby radius of deformation (10-40 km).

Figures 22 shows the satellite-derived and simulated distributions of chlorophyll at the surface for an annual mean. The model is able to represent the general pattern of chlorophyll with high values in upwelling regions and in the sub polar region. The satellite data was incomplete at high latitudes (+/-50 degrees latitude). This is due to the fact that there are no winter values for chlorophyll. What is available for analysis is the average of the data. This may generate a seasonal

bias in the satellite data.

Additionally, the model captures the general distribution of higher primary production values and of higher seasonal variability in higher latitudes.



Figure 22: Sea surface chlorophyll from SeaWiFS satellite data compared to sea surface chlorophyll for Exp1.



Figure 23: Base 10 logarithm of the satellite chlorophyll versus the modeled control run chlorophyll.

Figure 23 shows the satellite chlorophyll data plotted against the modeled data. This was plotted logarithmically and is called the geometric mean. This is useful in removing outlying data points because chlorophyll is typically log normally distributed. There exists a relatively good correlation between the two sets of chlorophyll data.

There are some significant deficits in the representation of the ocean circulation, such as an overestimate of nutrient upwelling along the equator. The

Chapter 3: Results

model-based primary production is high in the equatorial regime, especially in the Equatorial East Pacific. Additionally, due to the models coarse resolution it misses the high chlorophyll areas along coastal boundaries that are due to coastal upwelling. The model is unable to capture the high chlorophyll values right near the coast that are apparent in the satellite data.

There are some limitations in how realistic the model can represent the effects of enhanced weathering due to the fact that the atmospheric CO_2 level is held constant at 370ppm, which is the atmospheric level of CO_2 in the year 2000. This is because we do not have a closed system, but instead have an open system with a prescribed CO_2 concentration. Carbon dioxide is being "removed" from the atmosphere and transferred into the ocean, but the atmospheric p CO_2 in the model is not reduced, it is instead held at a fixed level. Adding a varying atmospheric CO_2 concentration would make for a more realistic scenario.



Figure 24: A. The total diatom surface chlorophyll per year, averaged over the five-year control run. B. The total small phytoplankton chlorophyll for one year, averaged over the fiver-year control run.

The total chlorophyll, diatom chlorophyll (Fig. 24A) and small phytoplankton (Fig. 24B) are shown as a sum of the total chlorophyll per year averaged over the five-year control run. The total chlorophyll and diatom chlorophyll both have highs in the Eastern Equatorial Pacific and in the coastal regime. Both the total surface chlorophyll and the diatom chlorophyll have maximum values of around 2 mg/m³.

The diatom and total chlorophyll patterns match due to the fact that the diatom chlorophyll has a much larger contribution to the total surface chlorophyll than the small phytoplankton, with diatom chlorophyll making up about 75% of the total surface chlorophyll. The small phytoplankton has peaks in the western equatorial

Pacific and in the Indian Ocean with a maximum value of about 0.55 mg/m³. The small phytoplankton seem to dominate in the subtropical gyres, while diatoms are dominant in the subpolar gyres.



Figure 25: Validation data for Sea Surface pCO₂ compared to the Sea Surface pCO₂ for Exp1.



Figure 26: A. The total air-sea CO₂ flux per year for the control run, averaged over the five-year period. A negative flux represents a flux into the ocean. B. The average pH of the ocean surface water averaged over the five-year control run.

Figure 25 shows the derived surface pCO_2 data and the simulated surface pCO_2 data for an annual mean. The pCO_2 validation data was constructed through a combination of measured pCO_2 values normalized to a common year, 1995. The data was normalized based on an assumption on how much the pCO_2 changes per year and then interpolated temporally.

Similar to the chlorophyll distribution, there are high values for both pCO_2 (Fig. 25) and CO_2 flux (Fig. 26) out of the ocean near the equator. On the other hand, the

relatively high amount of diatom chlorophyll in the subpolar gyres of the North Atlantic and North Pacific corresponds to the lowest values for pCO_2 and CO_2 flux into the ocean. In the control run the ocean has an average sea surface pCO_2 of about 360 µatm with high values in areas with a high amount of upwelling and a high amount of primary production. The control run has an average pH of about 8.1, with the lowest pH corresponding to the highest sea surface pCO_2 .



3.2 Even Olivine Input Over the open Ocean (Exp2)

Figure 27: Top-Left: Change in Air-Sea CO₂ flux that occurs when olivine is distributed into the Earth's rivers. Top-Right: Change in sea surface pCO₂. Bottom: Change in sea surface pH.

The focus of the analysis will be mostly on the open ocean distribution scenario due to the fact that the other scenarios require longer run times to stabilize.

For Exp2 a significant change in the CO_2 flux into the ocean is seen. For CO_2 flux there exists a temporal saturation tendency, while there is a fairly linear increase

in flux with respect to olivine input. It appears that the input of olivine (every year) takes a few years until it has reached its full efficiency. The temporal saturation can be seen best in the 10 petagram input run (Exp2.4), where the curve seems to be approaching a maximum at about 2.14 PgC / yr. Using this value, the efficiency is estimated at roughly 0.214 petagrams of carbon per petagram of olivine, and is fairly constant with the varying amount of olivine input.

Under a sustained constant input flux of olivine, there is an increasing uptake of CO_2 by the ocean (Fig. 27A) with time that tends to a constant annual flux. This increase may not be completely stationary, even at the end of the five-year run as the CO_2 flux may not have reached a stable state. The CO_2 flux in the final year of the experimental runs scales approximately linear with the input of Olivine, but there appears to be small amount of saturation. The slope, or the efficiency of sequestration, is roughly 0.214 Pg C / Pg Olivine.

The pattern both in the temporal evolution of pCO_2 for a single experiment and between the experiments very closely mimics the pattern in air-sea CO_2 flux. This change is pCO_2 (Fig. 27B) is expected as the change in pCO_2 controls the change in CO_2 flux. The pCO_2 scales fairly linearly with olivine added, but shows saturation with time. With 1 petagram of olivine input there is an average decrease in pCO_2 by 0.10 µatm, with a significantly larger decrease, about 1.08 µatm, for 10 Pg due to the increase in total alkalinity.

As expected, the increase in olivine input leads to an increase in sea surface pH. The pH across the entire ocean is increased by an average of 0.0145 for an input of 10 petagrams of olivine (Exp2.4). There was a slight increase in pH across most of the ocean. High productivity areas, such as the opal belt in the Southern Ocean and in the equatorial Pacific, experienced a greater increase in pH. The change in pH scales linearly with the amount of olivine distributed.

In the 2-D plots for CO_2 flux, pCO_2 , and pH (Fig. 28) it is evident that areas, such as the Eastern Equatorial Pacific, that have an increase in the amount of CO_2 flux into the ocean correspond with a decrease in pCO_2 and a decrease in pH. The opposite is also true; a decrease in CO_2 flux corresponds with an increase in pCO_2 and an increase in pH.

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Figure 28: For (Exp2.3 – Exp1) – A. The change in total air-sea CO₂ flux per year for the control run, averaged over the five-year period. A negative flux represents a flux into the ocean. B. The change in the average pCO₂ of the sea surface in uatm. C. The change in average pH of the ocean surface water averaged over the fiveyear control run.

The vertical integral of primary production (Fig. 29A) has been computed over the entire water column to compare to the control run. The change in primary production shows an immediate response to olivine input, with no delay in the annual averages. There are strong correlations between primary production and silicate availability. In contrast to the CO_2 air-sea flux, a saturation point with respect to the amount of olivine input exists: while 1 Pg Olivine produces 0.43 PgC net primary production (a ratio of 0.43), 2 Pg Olivine causes only 0.63 PgC (a ratio of 0.33), 5 PgC Olivine causes 1.17 PgC (ratio 0.23) and 10 Pg Olivine causes 1.87 PgC (ratio 0.19).



Figure 29: Left: The change in net primary production. Right: Change in export production at 100 meters.

The carbon export production (Fig. 29B) was calculated at a depth of 85.7 meters. The carbon export variability is negatively correlated with the primary production variability. Generally, as primary production increases, export production decreases. The average decrease in export production in the final year of Exp2.4 is about 0.26 Pg C / yr (-2.92%) with the export production trending towards a further decrease in the future.

The detritus, summed over the whole ocean, integrated over depth and averaged over the five-year run, decreased by 4.32×10^{14} (1.14%) for the run with a flux of 5 Pg olivine and by 7.27 x 10^{14} (1.92%) for the 10 Pg run (Fig. 30). This decrease in detritus must be a result of an unexpected ecosystem reaction. The reduction in detritus could be a result of: less mortality of diatoms/small phytoplankton, less zooplankton feces, or from more efficient feeding of the zooplankton. The mortality rate of diatoms/small phytoplankton is calculated by:

 $mortality = aggregationRate * C_{phytoplankton} + aggregationRate * C_{diatom}$ [3.1] where the aggregation rate is determined by the loss of phytoplankton and diatoms (interaction amongst phytoplankton cells) and a product of phytoplankton with diatom and detrital biomass [Schartau et al., 2007].

An increase in mortality was not the cause of the decrease in export production because a small increase in the mortality rate with the addition of olivine is generated. There was a 4.35% increase in the rate of mortality with an input of 10 Pg olivine, averaged over the five-year simulation.

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Figure 30: The change in total water column detritus for Exp2.3 and Exp2.4 compared to Exp1.

Even though there was an increase in the rate of zooplankton grazing, there was a decrease in zooplankton feces. The decrease in zooplankton feces may be the cause of the decrease in export production. This was calculated with the following:

$$zoo_{feces} = hetLossFlux * recipQZoo$$
 [3.2]

$$hetLossFlux = 0.05 * N_{zoo} * N_{zoo}$$
[3.3]

$$recipQZoo = \frac{C_{zoo}}{N_{zoo}}$$
[3.4]

There was a reduction in the amount of zooplankton feces by an average of 5.0% for 10 Pg of olivine and by 2.5% for 5 Pg of olivine. Furthermore, a 1.32% decrease in the zooplankton biomass for 5 Pg olivine input and a 2.04% decrease for an input of 10 Pg olivine is observable.

The reduction in zooplankton biomass may be linked to the reduction in phytoplankton biomass. The phytoplankton biomass is reduced on average by 3.01% for 5 Pg of olivine input and by 4.70% for 10 Pg olivine input. On the other hand, diatom biomass increases with the amount of olivine added. A flux of 5 Pg olivine leads to an increase in the diatom biomass by 21.83% while a flux of 10 Pg olivine leads to a 30.71% increase in diatom biomass.

The ecosystem is a nonlinear system due to non-linear spatial distribution, stirring, and various non-linear interactions between biological components (e.g. interactions between species). There are some significant non-linearities in the biological pump: primary production increases slightly, and more or less linearly with year and weathering intensity, but export production is clearly nonlinear, decreasing

as more olivine is added. It is evident from the figures given for the diatom and small phytoplankton biomass that a significant shift in species composition exists as a result of olivine distribution.



Figure 31: A. The change in limitation due to nitrogen availability for Exp2.4 compared to Exp1. B. The change in limitation due to iron availability for Exp2.4 compared to Exp1. C. The change in the small phytoplankton growth rate summed over the entire water column for Exp2.4 compared to Exp1.

A significant drop in small phytoplankton growth rate (Fig. 31C) when there is an input of olivine into the ocean can be seen. This may also lead to a decrease in the export production as the zooplankton grazing depends heavily on the phytoplankton biomass. The decline in small phytoplankton growth rate is not due to nutrient limitation as both nitrogen (Fig. 31A) and iron (Fig. 31B) are less limiting as more olivine is added. The decline in growth rate is instead due to being outcompeted by diatoms.

The average diatom surface chlorophyll (Fig. 32A) increased (mg/m³). The only significant decrease in diatom biomass occurred along the southwestern border

Chapter 3: Results

of South America and in the Southern Ocean in the subpolar gyres. The greatest increase of diatom chlorophyll came in the equatorial Pacific. The mid latitudes from 40°S to 40°N experienced a fairly uniform increase in diatom chlorophyll of about 0.3 mg/m³.



Figure 32: For (Exp2.3 – Exp1) - A. The change in total diatom surface chlorophyll per year, averaged over the five-year control run. B. The change in total small phytoplankton chlorophyll for one year, averaged over the fiver-year control run.

Conversely, the average small phytoplankton surface chlorophyll (Fig. 32B) was greatly reduced. Across the mid latitudes from 40°N to 40°S, the small phytoplankton was reduced by an average of 1.5 mg/m³. There was an exceptionally high area of small phytoplankton chlorophyll reduction in the Eastern Equatorial Pacific, which roughly coincides with the area of high diatom chlorophyll increase. Along the coasts and in the higher latitudes, small phytoplankton chlorophyll values remained roughly the same. The amount of small phytoplankton chlorophyll experienced a minimal increase in the subpolar gyres.

The e-ratio (Fig. 33), which describes the efficiency of the biological pump, is reduced as olivine is added. The efficiency of the biological pump is 28% for the 10 Pg olivine input scenario, which is a decrease in the efficiency compared to Exp1. It is also important to note that the change in the export of CaCO₃ is significant due to the shift away from calcifiers towards diatoms. The decrease in CaCO₃ export scales linearly with olivine input with a decrease of about 0.05 Pg CaCO₃ export per petagram of olivine. The decrease in CaCO₃ export is linear with time and shows no saturation, with the curve trending towards a further decrease in CaCO₃ export in the final year. This will also play a role in the decrease in export production as calcifiers

play an important role in the export of carbon to the deep ocean. The quantities of interest and the change in these quantities are shown in Table 5.



Figure 33: The e-ratio, which describes the efficiency of the biological pump, is reduced as more olivine is added.

yedi.								
	Exp2.1	Exp2.2	Exp2.3	Exp2.4				
Change in Primary Production (PgC yr ⁻¹)	0.43	0.66	1.17	1.87				
% change	1.48%	2.27%	4.03%	6.45%				
Change in Export Production (PgC yr ⁻¹)	-0.06	-0.13	-0.23	-0.26				
% change	-0.67%	-1.46%	-2.58%	-2.92%				
Change in CaCO₃ Export (Pg yr ⁻¹)	-0.054	-0.098	-0.203	-0.325				
% change	-9.84%	-17.79%	-36.85%	-59.10%				
Change in CO₂ Flux into the Ocean (PgC yr ⁻¹)	0.20	0.41	1.04	2.14				
% change	13.7%	28.1%	71.2%	146.6%				
Change in pH	0.0014	0.0029	0.0073	0.0145				
% change	0.017%	0.036%	0.090%	0.179%				
Change in Sea Surface pCO₂ (uatm)	-0.10	-0.21	-0.54	-1.08				
% change	-0.028%	-0.060%	-0.154%	-0.308%				

 Table 5: Values for changes in important variables for (Exp2 - Exp1).
 All values are averaged over the final

Exp5: Even Distribution without Alkalinity Flux

The Exp5 distribution scenario involved the even distribution of silicate over the open ocean. This differed from Exp2 in that it did not include the flux of alkalinity that would result from the olivine dissolution reaction.

There are two effects contributing to the sequestration of carbon: the changes in ocean chemistry due to alkalinity input and the increased NPP, export and biological pump due to Si input. Both of these mechanisms contribute to a varying degree to the overall effect of C sequestration.

Exp5 is useful in illustrating to what extent these different carbon sequestration mechanisms act. This is an auxiliary experiment used to check the role of the biology without alkalinity flux. The primary production and the carbon export associated with Exp5 is the same as that associated with Exp2 due to the same input of Si. A significant decrease in CO_2 flux into the ocean compared to that in Exp2 can be observed. The change in flux relative to Exp1 becomes positive at the end of the five year signifying oceanic outgassing of CO_2 to the atmosphere.

Here, the air-sea CO₂ flux (Fig. 34A) represents the amount of CO₂ flux that the biological pump accounts for. Without the flux of alkalinity the sequestration efficiency is greatly reduced to less than 10% of the situation in Exp2, with the airsea CO₂ flux at times contributing towards an increase in the outgassing to the atmosphere. In the final year of simulation, on average a flux of 1 Pg olivine leads to a negative drawdown (outgassing) of only -0.01 Pg of C, 2 Pg olivine sequesters -0.01 Pg C, 5 Pg olivine sequesters 0.02 Pg C and 10 Pg olivine sequesters 0.10 Pg C. The change in carbon flux due to the change in the ocean's biology is negative at some points in the year and this would contribute to outgassing to the atmosphere. The carbon flux due to the the biological changes is very non-linear in both time and with respect to the amount of olivine distributed. As more olivine is added the effect of the just silicate distribution on the CO₂ flux changes from a negative effect to a positive effect. Even though there is an observed increase in CO2 flux into the ocean in some iterations of Exp5, the effect of the biological pump on CO2 flux continues to be negative as is evident by the continuing decrease of the carbon export production.

Similarly to CO_2 flux, a significant decrease in the change in sea surface p CO_2 (Fig. 34B) is apparent when there is no alkalinity flux. Nevertheless, the pattern of p CO_2 distribution, both in the temporal evolution of a single experiment and between



the experiments, is very similar to that of carbon uptake.

Figure 34: Top-Left: Change in Air-Sea CO₂ flux that occurs due to even distribution of only silicate. Top-Right: Change in sea surface pCO₂. Bottom: Change in sea surface pH.

The sequestration rate due to only the biological pump suggests that the sequestration due to alkalinity change is responsible for most of the increase in CO_2 flux. The change in oceanic chemistry accounting for a large portion of the increase in carbon flux into the ocean ranging from 0.2 Pg C per 1 Pg Olivine and scales linearly with the flux of olivine.

X	∆DIC(Exp2.x)	%DIC(Exp2.x)	∆DIC(Exp5.x)	%DIC(Exp5.x)
1	+1.59 x 10 ¹⁵	+0.05%	+5.48 x 10 ¹⁴	+0.02%
2	+3.02 x 10 ¹⁵	+0.10%	+9.52 x 10 ¹⁴	+0.03%
3	+7.08 x 10 ¹⁵	+0.22%	+1.91 x 10 ¹⁵	+0.06%
4	1.33 x 10 ¹⁶	+0.42%	+3.07 x 10 ¹⁵	+0.10%

Table 6: Change in DIC. All values are averaged over the simulation run time of five-years.

With both Exp2 and Exp5 the DIC increases fairly uniformly with time and with olivine input amount. But, there is a much greater increase in DIC for Exp2 due to the alkalinity flux. DIC is the sum of all inorganic carbon species, thus a greater flux of bicarbonate will lead to a greater increase in DIC (Table 6).

3.3 Results for Riverine (Exp3) and Ship (Exp4) Distribution

The experiment with riverine produces less change in all parameters. This is due to the localized input of silicon and alkalinity in this distribution scenario, which is not transported throughout the ocean. The ships of opportunity distribution scenario produces results similar to that of the even distribution scenario. To see the final results for these scenarios one might need longer runs here.



Figure 35: Top-Left: Change in Air-Sea CO₂ flux that occurs when olivine is distributed into the Earth's rivers. Top-Right: Change in sea surface pCO₂. Bottom: Change in sea surface pH.

The air-sea CO_2 flux (Figs. 35A & 36A) qualitatively corresponds to expectations, with the efficiency of CO_2 drawdown (averaged over the final year of

simulation) compared to olivine input being the lowest for riverine input (around 0.12 PgC/Pg olivine), somewhat higher for ship input (around 0.214 PgC/Pg olivine), and about the same (about 0.214 PgC/Pg olivine) for uniform input. The river input scenario still has a trend towards higher CO_2 uptake after the five year run.

The average pCO_2 decreases by a similar ratio as CO_2 flux (Figs. 35B & 36B). Exp3 is trending towards lower pCO_2 levels at the end of the five-year run, while Exp4 is leveling off similar to Exp2.



Figure 36: Top-Left: Change in Air-Sea CO₂ flux that occurs when olivine is distributed into the Earth's rivers. Top-Right: Change in sea surface pCO₂. Bottom: Change in sea surface pH.

In the surface plots (Fig. 37) it is easy to see the localization effect of the olivine distribution. For Exp3 much of the ocean is left unaffected, with the changes being localized to the mouths of the two largest rivers, The Amazon River and The Congo, and to the Bay of Bengal. These areas experience a rise in the amount of CO_2 entering the ocean (Fig. 37A) caused by a reduction in the sea surface p CO_2 (Fig. 37B). The olivine dissolution in the localized areas also leads to an increase in

the pH (Fig. 37C).



Figure 37: For (Exp3.3 – Exp1) - A. The change in total air-sea CO₂ flux per year for the control run, averaged over the five-year period. A negative flux represents a flux into the ocean. B. The change in the average pCO₂ of the sea surface in uatm. C. The change in average pH of the ocean surface water averaged over the fiveyear control run.

For Exp4, the changes are more broadly dispersed than Exp3, but still localized to the more popular shipping routes (Fig. 38). A significant effect due to olivine distribution can be seen in the Northern Atlantic between North America and Europe. In Exp4 it is still possible to see a significant change in the Equatorial Pacific that dominates in Exp2. This area in the Equatorial Pacific has high values in CO₂ flux (Fig. 38A) into the ocean resulting from a high pCO₂ (Fig. 38B) and thus leading to a reduction in the pH of the surface waters (Fig. 38C).



Figure 38: For (Exp4.3 – Exp1) - A. The change in total air-sea CO₂ flux per year for the control run, averaged over the five-year period. A negative flux represents a flux into the ocean. B. The change in the average pCO₂ of the sea surface in uatm. C. The change in average pH of the ocean surface water averaged over the fiveyear control run.

Exp3 has lower values of increased net primary production due the less widespread distribution of olivine (Exp 39A & 40A). Thus, many areas of the ocean are still silicate limited. The same pattern of distribution due to localized input in Exp3 as for CO₂ flux and pCO₂, but with a less significant effect, also holds for the primary production and for the export production. Exp4 has similar values for primary production and export production as seen in Exp2. No matter what distribution scenario is used, olivine distribution lead to an increase in primary production (Figs. 39A & 40A) and a decrease in export production (Figs. 39B & 40B). Surprisingly, but similarly to Exp2, an increase in the primary production has lead to a decrease in the export production.

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Figure 39: Left: The change in net primary production. Right: Change in export production at 100 meters.



Figure 40: Left: The change in net primary production. Right: Change in export production at 100 meters.

The area where primary production and export production are effected by olivine distribution is very localized. The effect seen is the same as for Exp2, specifically the amount of diatom surface chlorophyll increases (Figs. 41A & 42A) and the amount of small phytoplankton surface chlorophyll decreases (Figs. 41B & 42B) where olivine has been dissolved. This is illustrative of the species shift that could be a result of olivine distribution.



Figure 41: For (Exp3.3 – Exp1) - A. The change in total diatom surface chlorophyll per year, averaged over the five-year control run. B. The change in total small phytoplankton chlorophyll for one year, averaged over the fiver-year control run.



Figure 42: For (Exp4.3 – Exp1) - A. The change in total diatom surface chlorophyll per year, averaged over the five-year control run. B. The change in total small phytoplankton chlorophyll for one year, averaged over the fiver-year control run.

3.4 Long-Term Effects

The figures for the long-term run (Exp6) are shown in absolute numbers since there was no long-term control run for comparison. This log-term run was conducted using an input of 5 Pg of olivine. All figures are displayed as absolute values and not as difference values relative to a control run. The CO₂ flux (Fig. 43A) into the ocean increases quickly in the first five years, after which it continues to increase for the next 25 years, but at a slower rate, eventually reaching a maximum of 10 Pg CO₂ per year. This does not signify an increase in CO₂ flux by 10 Pg CO₂ per year, but instead shows the total CO_2 flux. This would result in an increase of CO_2 flux into the ocean of approximately 5 Pg CO_2 yr⁻¹, which is a 1:1 ratio for PgC : Pg Olivine. After 30 years the system appears to reach a saturation point and at 35 years the efficiency of the carbon sequestration begins to decrease.

The primary production and export production are both trending towards increases, but are slowly stabilizing (Figs. 43B & 43C). Previous results show that the carbon export decreases as olivine is added. This is the case here as well, but is not observed since what is represented here are absolute values, not relative values compared to a control run. The increase in the export production is due to natural drift in the model and the export production will continue to increase, but will also continue to be smaller than the export production seen in the control run.



Figure 43: Trends for the long-term run (Exp6). A. The air-sea CO₂ flux in grams CO₂ per year. A negative number signifies flux of CO₂ into the ocean. B. The long-term trend for primary production in grams Carbon per year. C. The long-term trend of carbon export production in grams Carbon per year.
Chapter 4: Discussion

4.1 Outline

In a recent report published by The Royal Society (2009) many geoengineering options were evaluated. The Royal Society summarized the validity of each option based on effectiveness, safety, cost, and timeliness. Enhanced weathering was found as a method that would be highly effective and very safe, but would be very costly and take a long time to implement (Fig. 44).



Figure 44: According to the Royal Society enhanced weathering as a geoengineering option has high effectiveness and is very safe, but has low affordability and proceeds slowly [source: The Royal Society, 2009].

These four means of evaluation are important to keep in mind when evaluating any proposed geoengineering method.

4.2 Effectivity of Enhanced Weathering

In theory, enhanced weathering of olivine should be very effective because it acts upon both the long-term and short-term carbon cycles, acting via multiple mechanisms to increase carbon dioxide transport into the ocean. The fact that CO₂ is to be sequestered back into the slow, long-term carbon cycle is most important as this necessary for carbon sequestration to work as a climate mitigation strategy [Chisholm et al., 2001]. While we see an increase in carbon flux into the ocean due

to the change in ocean chemistry, we see a reduction in the amount of carbon sequestered through the biological pump.

Net Effect

Under a sustained flux of olivine there is an increase in the uptake of CO₂ by the ocean. The change in CO₂ flux per petagram of olivine is increasing as the amount of olivine input increases. For even distribution over the open ocean, the ratio of carbon sequestered per olivine distributed in 10 petagram distribution scenario (Exp2.4) is 1 Pg olivine per year increases the CO₂ flux by a maximum of 0.214 PqC yr⁻¹. This corresponds to a maximum carbon dioxide drawdown of about 0.8 PgCO₂ per Pg Olivine. This value of 1:0.8 is lower than the values found by previous research: 1:1.25 [Schuiling & Krijgsman, 2006] and 1:1 [Köhler et al., 2010] and compared to the theoretical value of 1:1.25. The increasing ratio of carbon sequestered per amount of olivine distributed is due to the biological effects of silicate distribution. When lower amounts of olivine are distributed (1 and 2 petagram scenarios) the ocean biology has a negative impact on carbon sequestration. On the other hand, when the higher amounts of olivine are distributed (5 and 10 petagram scenarios) the biology begins to have a positive impact on the carbon sequestration. This biological impact does not signify an increase in the biological pump, but is instead likely due to the change in ocean chemistry that results in the increased amount of primary production. The alkalinity distribution is responsible for the majority of the carbon sequestration and scales linearly with the amount of olivine distributed.

The olivine dissolution reaction itself consumes carbon dioxide. During the chemical weathering process of olivine CO_2 is removed from the atmosphere. Atmospheric CO_2 reacts with rainwater to form carbonic acid and then chemically dissolves the olivine [Köhler, 2010]. The reaction products are silicic acid, magnesium ions and bicarbonate. Bicarbonate is the predominant chemical form in which dissolved CO_2 exists in the ocean [Köhler, 2010]. Four moles of CO_2 are consumed while 4 moles of bicarbonate are produced.

Olivine dissolution increases the concentration of bicarbonate thus increasing the total alkalinity. The increase in alkalinity lowers the partial pressure of carbon dioxide in the water (and increases the buffering capacity) and leads to a further uptake of CO_2 by the ocean surface due to gas exchange (Köhler et al., 2010). According to Kheshgi (1995) increasing the total alkalinity by one mole increases the carbon content of the ocean by 0.89 moles. The CO_2 flux in the ocean due to

alkalinity accounts for almost all of the increase in CO_2 flux. A comparison of the CO_2 flux rate achieved with a flux of alkalinity to the CO_2 flux rate without a flux of alkalinity shows that the change in oceanic chemistry accounts for most of the increase in CO_2 flux into the ocean for the five-year run of Exp2.4. CO_2 flux due to alkalinity distribution account for 0.2 Pg C / Pg olivine of flux into the ocean. The CO_2 flux due to the alkalinity distribution scales linearly with the amount of olivine distributed.

It was expected that more available silicate in the ocean would lead to an increase in the biological pump due to a stimulation of diatom growth, but this was not the case. Tsuda et al. (2005) found in their research that when diatom growth is stimulated, the higher biomass or production of primary producers caused higher export production. Furthermore, the increase in diatom production is expected to facilitate particle aggregation and accelerate sinking processes [Passow, 2002]. The results from this study show that the aggregation rate is actually decreased as the flux of olivine increase. Diatoms have been considered to play a large role in the biological pump because they contribute to a large fraction of export production [Goldman, 1993; Sarmiento & Gruber, 2006].

While the biological pump is negatively affected, the input of only silica (Exp5) still lead to a positive change in the CO_2 flux into the ocean for some iterations of Exp5. The 5 petagram (Exp5.3) and 10 petagram (Exp5.4) iterations lead to a minor increase in the amount of CO_2 entering the ocean in the final year of the experimental run. This small increase is not due to an increase in the biological pump, as the carbon export production continues to decrease, but instead is most likely due to oceanic chemistry changes that are a result of the increased amount of biological primary production.

An increase in the primary production was observed for all distribution scenarios, showing saturation with increasing olivine input. This means that the input of Si is meeting fewer diatoms that are Si limited. Thus, adding more Si than the diatoms can utilize does not lead to a further increase in their growth.

The behavior of the carbon export is the most interesting and unexpected. It was expected that the pattern in primary production variability would be transferred to the variability in export production. Following that logic, an increase in primary production would lead to the production of more detritus and more carbon export production [Schneider et al., 2008]. In the model simulation, the increase in primary production actually had the opposite effect; there was a decrease in detritus as more

olivine is added across all the distribution scenarios. Counter to what is expected, the diatom bloom leads to a decrease in aggregation rate and thus a decrease in the sinking of detrital particles.

An increase in diatom biomass and a decrease in phytoplankton biomass are observed. This supports findings from recent studies that suggest that calcifiers (small phytoplankton) play a more important role in transferring carbon to depths [Francois et al., 2003; Klaas & Archer, 2002]. My results show that the declining export production corresponds with declining amounts of $CaCO_3$ export, further supporting the theory that calcifiers play a more important role in export production that the declining hand the theory that calcifiers play a more important role in export production that the declining the theory that calcifiers play a more important role in export production than diatoms.

The increase in net DIC may also shed some light on the reduction in the export production. According to Köhler et al. (2010) as olivine is added the alkalinity will increase, but the net DIC should remain constant. Contrary to this, an increase in DIC content is observed in my model. According to previous studies, the observed increase in DIC in the simulations could be due the fact that the majority of carbon fixed by phytoplankton is remineralized by bacteria and zooplankton [Buesseler, 1998; Boyd et al., 2004]. The observed increase in zooplankton grazing supports the idea that a majority of the fixed carbon is remineralized in the surface waters. This would lead to less of the dead material sinking out of the photic zone.

The decrease in export seems to be most highly correlated with the change in phytoplankton biomass. While the export certainly experiences a decrease with increasing olivine input, the overall impact of the decrease is questionable with the maximum decrease being very small, an average of -2.92% (-0.26 PgC) over the final year of the five-year run of Exp2.4. Previous studies have also found that only a small fraction (8%) of the fixed carbon due to induced phytoplankton blooms sank to the deep ocean. This is significantly lower than the rate of export production observed in natural blooms [Buesseler, 1998].

Additionally, Zeebe and Archer (2005) demonstrate that the sequestration of CO₂ that occurs is on the order of 10-25% of the export production due to enhanced diatom blooms. This further reduces the theoretical amount of carbon that is permanently stored away from the atmosphere by the stimulation of the biological pump, showing that the inefficient vertical transfer of carbon from the surface to the deep ocean may greatly reduce the amount of carbon sequestered by the enhancement of the biological pump [Boyd et al., 2004].

It is obvious that biological variability plays a large role in the fate of carbon sequestration due to artificially induced phytoplankton blooms [Boyd et al., 2007]. Consequently, in order to understand the impact of the enhanced weathering on the biological pump further mechanisms have to be investigated.

It is important to note that since olivine dissolution was simulated via input of the dissolution products, the actual dissolution reaction and the factors that affect it were not taken into consideration. This is important because external factors may lead to a reduction in the rate of dissolution. According to Hangx and Spiers (2009) the higher oceanic pH will reduce the dissolution rate. As the pH increases the dissolution time of olivine will increase (Köhler et a., 2010). According to Schuling and Krijgsman (2006) for every increase/decrease of the pH by 0.3 units, the amount of time needed to weather the olivine is doubled/halved respectively. These varying conditions were not accounted for in my model, as the application of silicate and alkalinity fluxes was constant with time and pH level.

Counteracting Acidification

This study shows that the dissolution of olivine counteracts the rising pH of the ocean. A flux of 10 Pg olivine leads to an average increase of 0.012 per year over the five-year simulation. The change in pH is trending towards an increase, but the rate of increase is slowing over the fiver year run. The pH of the surface water of the ocean was increased by 0.0145 in the final year of the simulation of Exp2.4 and was trending logarithmically toward a further increase in the future. Interpolating the results from Exp2.4 suggests that the input of 10 petagrams of olivine would lead to an increase in by pH by 0.03 by the year 2100. This is significantly smaller than the estimated increase in pH by Köhler et al. (2010). Additionally, dissolution characteristics will change as pH changes. Therefore, further investigation into the long-term effects on pH is still necessary.

Comparison of Distribution Scenarios

As expected, there is varying efficiency in the increase of carbon flux into the ocean amongst the distribution scenarios. Exp2 has the greatest efficiency in drawdown of CO₂ at approximately 0.214 PgC/Pg olivine (in the final year), the efficiency for Exp4 is a little lower but also around 0.214 PgC/Pg olivine and the efficiency for Exp3 is significantly lower at about 0.12 PgC/Pg olivine. Qualitatively this agrees with expectations, but a lower efficiency for the ship input scenario was expected. The even distribution scenario was expected to have a larger overall effect than the ship distribution scenario due to the fact that the olivine was distributed over

a larger area. Counter to this, the effects of the even distribution (Exp2) and ship distribution (Exp4) scenarios are almost identical. This is because in the ship distribution experiment the olivine is distributed in mostly the northern hemisphere where the water is silicate limited. The silicate that results from the olivine dissolution will then encounter more diatoms that require silicate. This is as opposed to the even distribution scenario where some of the olivine is distributed in water that has enough silicate. The extra silicate is 'wasted' in these areas because it does not encounter diatoms that require silicate and does not lead to an increase in primary production in these waters.

It is also observed that in the river scenario the CO_2 flux is still trending towards higher CO_2 uptake after 5 years, which is understandable, given that the plume of increased alkalinity needs more time to spread if its source is more localized.

The localized distribution of olivine may lead to the waters in the areas of distribution becoming saturated. Following the reasoning from Köhler et al. (2010) the input of olivine may be limited by the saturation of silicic acid and by controlling olivine input in the interest of maintaining safe pH levels.

Long-Term Effects

I conducted a very brief investigation into the long-term trends that result from the enhanced weathering of olivine. The enhanced weathering leads to a continued flux of CO₂ into the ocean for the first few decades of application, after which it will reach a saturation point and the efficiency of carbon sequestration will begin to be reduced. The pCO₂ continues to closely mimic the CO₂ flux's variations with time and olivine input. As Cullen and Boyd (2008) pointed out, it will be necessary to predict and verify long-term effects of geoengineering proposals, but it may not be possible to detect all significant effects, such as anoxia and gas emissions against the background ocean variability [Strong et al., 2009]. Exp6 was done to gain a glimpse into long-term effects, but a significant amount of research into this is still required.

4.3 Safety of Enhanced Weathering

On the first order, the only significant consequence resulting from olivine fertilization of the ocean is the high pH resulting, but as mentioned earlier this is a benefit because increasing the pH of seawater will restore more normal conditions [The Royal Society, 2009; Köhler et al., 2010]. The sequestration of carbon through

Chapter 4: Discussion

olivine weathering provides additional benefits, such as the restoration of marine ecosystems [The Royal Society, 2009; Köhler et al., 2010]. The dissolution of olivine causes an increase in the total alkalinity (TA) of seawater by 4 moles per mole of olivine dissolved [Köhler, 2010]. This counteracts the danger of the ongoing acidification of the ocean.

While olivine fertilization of the ocean "mimics" a natural process it is in reality not natural at all. Olivine would be delivered to ecosystems at rates that do not mimic the natural process leading to some unknown possibly negative second-order consequences on the ecosystem [Chisholm et al, 2001].

The distribution of olivine into the Earth's oceans leads to an increase of phytoplankton in a water body. In the case of olivine, it leads to a large bloom of phytoplankton, specifically of diatoms, with many potential impacts on the ecosystem.

Diatom vs. Small Phytoplankton Species Shift

The distribution of olivine leads to a competitive advantage for certain species by making abundant the normally limiting nutrient, silicate. This process causes shifts in the phytoplankton community structure.

If implemented on a large scale, olivine distribution would change the ecology of the oceans. While enhanced weathering increases phytoplankton productivity and biomass, it changes the composition of the phytoplankton community with possible negative effects [Chisholm, 2001]. The enhanced weathering of olivine would not be environmentally benign causing, to a varying degree of severity depending on how much olivine is distributed, a shift away from small phytoplankton towards diatoms. Changes in the composition of the phytoplankton community are due to the elevated levels of silica that are a result of the weathering reaction of olivine. The elevated levels of silica favor diatoms, allowing them to out-compete other phytoplankton species.

The availability of silicate leads to a reduction in small phytoplankton growth rate and the small phytoplankton biomass (-4.70% for Exp.24), while the diatom biomass increases (+30.71% for Exp2.4). The reduction in small phytoplankton growth is not due to nutrient limitation as the availability of nutrients is less limited as more olivine is added. The reduction in growth can therefore only be due to small phytoplankton being outcompeted by diatoms due to silicate availability. The EIFEX experiment, which was conducted over 35 days and involved distribution of FeSO₄ to the Southern Ocean, shows a similar shift in phytoplankton species composition

[Hoffman et al., 2006; Jacquet et al., 2008]. The EIFEX experiment, among others, showed that a change in nutrient availability (particularly the availability of silicate) leads to a floristic shift away from small calcifying phytoplankton towards diatoms [Tsuda et al, 2005; Hoffman et al., 2006; Jacquet et al., 2008]. This agrees with my findings of a compositional shift towards diatoms.

Anoxia and Greenhouse Gas Production

The artificial enhancement of primary production would be expected to lead to possible anoxic zones due to an increase in sinking of dead material. The increase in available silicate leads to a bloom of diatoms. These diatom blooms would lead to light limitation on bottom-dwelling primary producers and decreases in the amount of oxygen available. Under conditions with sufficient nutrient levels, the amount of dissolved oxygen greatly increases during the day, but is greatly reduced after dark by phytoplankton respiration and by microorganisms that feed on the increasing amount of detritus. Sarmiento and Orr (1991) predicted a huge area of anoxia associated with phytoplankton blooms. Counter to this prediction, the results show that there may not be much oxygen depletion due to the fact that the amount of detritus available for bacterial decomposition is reduced. This is due to the fact that the change in the biological pump is working opposite to what was expected. The decrease in phytoplankton biomass generates less detritus in the water column and thus less sinking of dead detrital material to the deep ocean. Additionally, based on an initial, brief analysis there is an increase in the export of dissolved organic material to the deep ocean, which would lead to oxygen enrichment.

The distribution of ground olivine may trigger unknown effects on deep-sea life and thus on biogeochemical processes. It could lead to an increase in the microbial organisms that produce other greenhouse gases such as methane and nitrous oxide, which have much higher warming potentials than CO₂. Methane has 21 times the heat trapping effect of CO₂. Previous research on phytoplankton blooms predicted that there exists a high potential for methane production as a result of anoxia [Sarmiento and Orr, 1992]. The results from my experiments suggest that enhanced olivine weathering would not lead to these negative side affects due to a reduction in the amount of dead material that is exported to the deep ocean. A deeper look into the microbial community is necessary to evaluate these effects.

4.4 Costs And Implementation

Olivine is a cheap and widely available material, making up a large percentage of the Earth's mantle. Olivine is a major constituent of dunite complexes, which are mined in a number of countries and can be found on every continent on Earth.

An additional consideration is the costs of implementing such a geoengineering method. As estimated by Steen and Borg (2002), the cost of mining, milling and grinding of 1 ton of rock in large-scale mining is 6 Euro/ton [Steen & Borg, 2002]. According to Schuling crushed olivine from a small mine in Greenland costs 23€ per ton and it is expected that the cost of olivine will drop below 15€ per ton for large mines in low-wage countries [Schuiling & Krijgsman, 2006]. According to Schuiling, is carbon sequestration using olivine performs at its maximum theoretical efficiency then the cost per ton of CO₂ will then be around 18€/ton, as one metric ton of olivine captures 0.8 tons of CO₂. Even though the costs are not astronomical, the removal of atmospheric CO₂ using olivine sequestration will cost several hundred billion Euros annually, which is well below the cost of other methods [Schuiling & Krijgsman, 2006].

The amount of olivine necessary for these applications is huge and lies in the range of present day global coal mining [Köhler et al., 2010]. Implementation of enhanced weathering would require an operation on a global scale that will bring olivine mining from a minor commodity to the world's third largest mining sector, behind only coal and steel [Schuiling & Krijgsman, 2006].

Additionally, one may think the CO_2 and other greenhouse gases produced from the grinding, mining, and transport of olivine would offset the CO_2 sequestered by enhanced weathering. This is true only to a small extent; a more conservative estimate by Köhler et al. (2010) for the total expenditure is close to 10%, which gives a carbon sequestration efficiency of 90%.

4.5 Future Research

In general a more detailed assessment of the impact on the ecosystem is necessary before considering the implementation of enhanced weathering. I performed one long-term run as a way to explore the possible long-term ecological impacts. Before implementing enhanced weathering of olivine as a geoengineering

method it would be important to conduct both model studies and field studies on long time scales because ecological impacts and CO₂ mitigation are scale-dependent.

In the model runs used in this research the atmospheric CO_2 is preset at 370 μ atm and does not vary. This is the measured value for pCO₂ in the year 2000. The pCO₂ in the atmosphere continues to increase. This increase in pCO₂ and the negative CO₂ contribution of the olivine distribution experiment are not taken into account in the model. Adding a varying, interactive atmospheric CO₂ concentration that follows one of the IPCC emission scenarios, would provide further insight into the reaction to increasing atmospheric CO₂ levels. In order to achieve the current results from this thesis, it would be necessary to fertilize the ocean once every second. A study with a less constant and more realistic distribution of olivine and a varying level of atmospheric CO₂ would be useful in determining a more realistic potential of olivine weathering.

It is of great importance to further explore the changes to oxygen distribution as these changes could have extreme impacts, creating anoxic zones in the ocean that cannot support life. Understanding the biophysical climate feedbacks and cycling of non-CO₂ greenhouse gases such as methane is also important because the enhanced weathering of olivine could create conditions that allow greenhouse gas producing microbes to thrive.

Finally, it is important to continue to improve modeling capabilities. Improved modeling studies of the results and consequences at higher spatial resolution, and with better ecosystem parameterization, the inclusion of other greenhouse gases, and improved biogeochemistry would help to further increase our understanding of the enhanced weathering of olivine and other geoengineering proposal.

Chapter 5: Conclusions

5.1 Summary

The MITgcm ocean circulation model was coupled to the REcoM-2 pelagic ecosystem model to investigate the efficacy and impacts of the enhanced weathering of olivine in the open ocean. Three distribution scenarios were constructed: even distribution over the open ocean, riverine distribution, and distribution via ballast water of ships of opportunity. All scenarios were run for five years and compared analytically to a control run. The analysis mainly focused on the results from the open ocean distribution due to the fact that the other two scenarios have a localized flux of olivine and require more time for the effects to reach a stable point where the olivine is dispersed.

Under a sustained constant flux of olivine, there is an increasing uptake of CO_2 by the ocean with time that tends to a constant annual flux. The maximum efficiency of the increase in carbon flux into the ocean is estimated at roughly 0.8 petagrams of carbon per petagram of olivine with the CO_2 flux in the final year of Exp2.4. This value is lower than the value found in previous research [Schuiling & Krijgsmann, 2006; Köhler et al., 2010] and lower than the value expected in this study and must be due to other mechanisms such as the negative effect of the biological pump and changes in the seawater chemistry due to increase CO_2 absorption. The amount of olivine scales approximately linearly with the input of Olivine. The effect from the change in alkalinity accounts for the majority of the increased CO_2 flux and is linear, while the biological effect is non-linear. The change in Sea surface p CO_2 follows the same temporal and spatial patterns as the change in CO_2 flux. The addition of bicarbonate to the ocean carbonate system due to the olivine dissolution reaction leads to a slight increase in the average pH across the ocean.

As expected the increased input of olivine leads to an increase in diatom productivity thus increasing the amount of primary production per year. The ratio of olivine to stimulated primary production decreased as more olivine was added (1 Pg olivine leads to +0.43 PgC PPI while 10 PgC leads to +1.87 PgC PPI). There is a saturation point in the increase in primary production signifying that as the silicate flux increases, it is reaching fewer diatoms that are silicate limited. This dynamic of a point of diminishing returns is important as an indicator that long-term studies are needed. The availability of silicate allowed diatoms to outcompete phytoplankton

leading to a shift in species composition with a reduction in small phytoplankton biomass (-4.70% for 10 Pg olivine) and an increase in diatom biomass (+30.71% for 10 Pg olivine).

The decrease in small phytoplankton leads to a reduction in the zooplankton biomass (-2.04% for 10 Pg olivine) and a reduction in total detritus integrated over the water column (-1.92% for 10 Pg olivine). This unexpected behavior leads to effects that are counterintuitive, specifically a decrease in the carbon export production. Carbon export production is reduced by -2.92% for a flux of 10 Pg olivine. The decrease in export production is most likely attributed to the decrease in phytoplankton biomass due to the fact that calcifiers play an important role in the export of carbon to the deep ocean. The efficiency of the biological pump is greatly reduced (28% for 10 Pg olivine compared to 31% for the control run) as a result of increases in primary production with corresponding decreases in export production.

The biological pump was thought to contribute to an increase in the sequestration of carbon, but it actually leads to a reduction in CO₂ sequestration, trending towards outgassing. The change in seawater chemistry due to the flux of alkalinity is therefore the main mechanism responsible for carbon sequestration. Comparing the sequestration rate for runs with an alkalinity flux to the sequestration rate of runs without an alkalinity flux suggests that the input of alkalinity accounts for the majority of the carbon sequestration due to olivine distribution, approximately 0.2 PgC / Pg Olivine. The stimulation of the biology has only a very small effect on the total amount of carbon sequestered. The biological pump decreases as more olivine is put into the ocean, with a negative effect on the carbon sequestration. In the scenarios with a larger amount of olivine input (5 and 10 petagrams of olivine), the ocean biology leads to a small increase of carbon flux into the ocean. This is due to the fact that the biological activity causes a change in ocean chemistry, the effect of which is larger than the negative effect of the biological pump.

While this method will lead to an increase in the carbon dioxide flux into the ocean, it will not be trivial to implement. For carbon sequestration via enhanced weathering to have a globally relevant impact it would require substantial infrastructure construction, including large-scale mining and distribution of olivine. The scope of mining required is on the order of the of coal and steel and would make olivine the third most mined material behind those previously mentioned.

5.2 Conclusion

In conclusion the enhanced weathering of olivine has a large potential to reduce atmospheric CO_2 in magnitudes that are relevant for geoengineering applications. By sequestering carbon in the ocean it addresses the root cause of climate change and not just the symptoms. Additionally, it addresses the other major problem associated with rising levels of atmospheric CO_2 , ocean acidification. It is relatively safe, but may have negative effects on the marine ecosystem. Further research into the potential effects on the marine ecosystem is required.

Artificially enhanced silicate weathering is a potentially important element in the construction of a strategy to manage climate change. Even if the full potential of enhanced weathering is exploited, it will not be able to sequester all the CO₂ that is emitted by the burning of fossil fuels. It should therefore be used alongside other measures to ameliorate climate change and its impacts.

Using the artificially enhanced weathering of olivine still has many uncertainties, which must still be investigated, involving the potential ecological impact among other unknown effects. Nevertheless, compared to other CDR techniques olivine dissolution is very effective, considered relatively safe and moderately expensive.

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Bibliography

- Adcroft, A., C. Hill, J. Campin and J. Marshall (2004a). MIT Climate Modeling Initiative. Overview of the Formulation and Numerics of the MIT GCM. <u>http://paoc.mit.edu/cmi/ECMWF2004-Adcroft.pdf</u>.
- Adcroft, A., J. Campin, C. Hill, and J. Marshall (2004b). Implementation of an Atmosphere–Ocean General Circulation Model on the Expanded Spherical Cube. Mon. Wea. Rev., 132, 2845–2863.
- Aksnes, D.L., J.K. Egge, R. Rosland, and B.R. Heimdal (1994). "Representation of Emiliania huxleyi in phytoplankton simulation models – A 1st approach." *Sarsia*, 79: 291–300.
- Allen M.R., D. Frame, C. Huntingford, C. Jones, J. Lowe, M. Meinshausen, an N. Meinshausen (2009). "Warming caused by cumulative carbon emissions towards the trillionth tonne." *Nature*, 458: 1163–1166.
- Aluwihare, L.I. Photo. last viewed: 12 June, 2011. <http://iod.ucsd.edu/courses/sio280/documents/aluwihare_marine_carbon_cy cle_7nov08.pdf>
- Arakawa, A. and V.R. Lamb (1977). "Computational design of the basic dynamical processes of the UCLA General Circulation Model." *Methods of computational physics*, *17*: 174-265. Academic Press.).
- Archer, D (2010). The Global Carbon Cycle. Princeton University Press, Princeton, New Jersey, 2010.
- Bernard, C.Y., G.G. Laruelle, C.P. Slomp, and C. Heinze (2010). "Impact of changes in river nutrient fluxes on the global marine silicon cycle: a model comparison." *Biogeosciences*, 7(2): 441–453.
- Bopp, L., O. Aumont, P. Cadule, S. Alvain, and M. Gehlen (2005), Response of diatoms distribution to global warming and potential implications: A global

model study, Geophys. Res. Lett., 32, L19606, doi:10.1029/2005GL023653.

- Boyd, P.W., T. Jickells, C.S. Law, S. Blain, E.A. Boyle, K.O. Buesseler, K.H. Coale, J.J. Cullen, H.J.W. de Baar, M. Follows, and others (2007). "Mesoscale iron enrichment experiments 1993–2005: Synthesis and future directions." *Science* 315(5812): 612–617.
- Boyd, P.W., C.S. Law, C.S. Wong, Y. Nojiri, A. Tsuda, M. Levasseur, S. Takeda, R. Rivkin, P.J. Harrison, R. Strzepek, and others. (2004). "The decline and fate of an iron-induced subarctic phytoplankton bloom." *Nature* 428(6982): 549– 553.

Brumfiel, Geoff (2009). "Climate-control plans scrutinized." Nature, 461(7260): 19.

- Buesseler, K.O. (1998). "The decoupling of production and particulate export in the surface ocean." *Global Biogeochemical Cycles 12*: 297–310.
- Caldeira K. and L. Wood (2008). "Global and Arctic climate engineering: numerical model studies." *Philosophical Transactions of The Royal Society A, 366*: 4039–4056.
- Chisholm, S., P.G. Falkowski, and J.J. Cullen (2001). "Dis-Crediting Ocean Fertilization." *Science*, 294(5541): 309-310
- Conkright, M.E., S. Levitus, and T.P. Boyer; United States. National Environmental Satellite, Data, and Information Service. World Ocean Atlas 1994.
 Washington, D.C.: U.S. Dept. of Commerce, National Oceanic and Atmospheric Administration, National Environmental Satellite, Data, and Information.
- Crutzen P.J. (2006). "Albedo Enhancement by Stratospheric Sulfur Injections: A Contribution to Resolve a Policy Dilemma?" *Climate Change*, 77: 211–220.

- Cullen, J.J., and P.W. Boyd (2008). "Predicting and verifying the intended and unintended consequences of large-scale ocean fertilization.' *Marine Ecology Progress Series 364*: 295–301, doi:10.3354/ meps07551.
- Doney S.C., V.J. Fabry, R.A. Feely & J.A. Kleypas (2009). "Ocean acidification: the other CO2 problem." *Annual Review of Marine Science*, *1*: 169–192.
- Dunne, J.P, J.L. Sarmiento, and A. Gnanadesikan (2007). "A synthesis of global particle export fro the surface ocean and cycling through the ocen interior and on the seafloor." *Global Biogeochemical Cycles, 26*: GB4006
- Egge, J.K., and D.L. Aksnes (1992). "Silicate as regulating nutrient in phytoplankton competition." *Marine Ecology Progress Series,* 83: 281–289.
- Egge, J.K. (1998). "Are diatoms poor competitors at low phosphate concentrations?" *Journal of Marine Systems, 16*(3-4): 191–198.
- Emerson, S.R. and J.I. Hedges (2008). Chemical oceanography and the marine carbon cycle, Cambridge University Press, 2008.
- Eswaran, H., E. van den Berg, and P. Reich (1993). "Organic carbon in soils of the world." *Soil Science Society of America Journal*, *57*(1): 0361-5995
- Fabricius, K.E., Chris Langdon, Sven Uthicke, Craig Humphrey, Sam Noonan, Glenn De'ath, Remy Okazaki, Nancy Muehllehner, Martin S. Glas & Janice M. Lough (2011). Losers and winners in coral reefs acclimatized to elevated carbon dioxide concentrations *Nature Climate Change*, *1*: 165–169 (2011)
- Fennel K., M. Losch, J. Schroter, and M. Wenzel (2001). "Testing a marine ecosystem model: Sensitivity analysis and parameter optimization." *Journal of Marine Systems*, 28: 45–63, 2001.
- Francois, R., S. Honjo, R. Krishfield, S. Manganini (2002). "Factors controlling the flux of organic carbon to the bathypelagic zone of the ocean." *Global Biogeochemical Cycles, 16*(4): 1087

- Geider, R.J., H.L. MacIntyre, and T.M. Kana (1998). "A dynamic regulatory model of phytoplanktonic acclimation to light, nutrients, and temperature." *Limnology and Oceanography*, *43*(4): 679–694.
- Goldberg, P., Z-Y. Chen, W. O'Connor, R. Walters, and H. Ziock (2001). "CO2 Mineral Sequestration Studies in US." Proceedings of the first national conference on carbon sequestration, May 14-17, 2001, Washington, DC.
- Goldman, J.C. (1993). "Potential role of large oceanic diatoms in new primary production." *Deep Sea Research 40*: 159-186.
- Griffies, S., A. Biastoch, C. Boning, F. Bryan, G. Danabasoglu, E. Chassignet, M. England, R. Gerdes, H. Haak, R. Hallberg, W. Hazeleger, J. Jungclaus, W. Large, G. Madex, B. Samuels, M. Scheinert, C. Severijns, H. Simmons, A. Treguier, M. Winton, S. Yeager, and J. Yin (2008). Coordinated Ocean-ice Reference Experiments (COREs), *Ocean Modelling* 11: 59–74.
- Griggs, D.J. (2002). "Climate change 2001: The scientific basis." *Weather*, 57(8): 267-269.
- Gruber, N., M. Gloor, S.E. Mikaloff Fletcher, S.C. Doney, S. Dutkiewicz, M.J. Follows, M. Gerber, A.R. Jacobson, F. Joos, K. Lindsay, D. Menemenlis, A. Mouchet, S.A. Muller, J.L. Sarmiento, and T. Takahashi (2009). "Oceanic sources, sinks, and transport of atmospheric CO2." *Global Biogeochemical Cycles*, 23(1): 1-21.
- Gupta, L.A. V. Subramanian and V. Ittekot (1997). "Biogeochemistry of particulate organic matter transported by the Godavari River, India." *Biogeochemistry*, 38(2): 103-128.
- Hangx, S.J.T., and C.J. Spiers (2009). Coastal spreading of olivine to control atmospheric CO2 concentrations: A critical analysis of viability. *International Journal of Greenhouse Gas Control*, 3(6), 757-767.

- Hedges, J.I. (1992). "Global biogeochemical cycles: progress and problems." Marine Chemistry, 39(1-3): 67-93.
- Herzog, H. (2002). "Carbon Sequestration via Mineral Carbonation: Overview and Assessment." MIT laboratory for Energy and the Environment, Cambridge, Massachusetts, 14 March.
- Hoffmann, L.J., I. Peeken, K. Lochte, P. Assmy, and M. Veldhuis. 2006. Different reactions of Southern Ocean phytoplankton size classes to iron fertilization. *Limnology and Oceanography* 51(3):1,217–1,229.
- Hohn, S. (2008). "Coupling and decoupling of biogeochemical cycles in marine ecosystems." *Ecological Modelling*.
- Huijgen, W.J.J. and R.N.J. Comans (2003). "Carbon dioxide sequestration by mineral carbonation." *Energy, ECN-C--03*: 1-52
- Huijgen, W.J.J., B.J. Witkamp, and R.N.J. Comans (2005). "Mineral CO2 Sequestration by Steel Slag Carbonation." *Environmental Science Technology*, 39I: 9676-9682
- IMCS, Ocean Modeling Group. Photo. last viewed: !8 May, 2011. <http://marine.rutgers.edu/po/documentation/docs.php?doc=romsman&page= technique&a=horizo ntal_grid>
- IPCC (2001). Climate Change 2001: The Scientific Basis. Cambridge University Press, Cambridge
- IPCC report (2007). Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate change (Cambridge Univ. Press, Cambridge, UK, 2007).
- Jacquet, S.H.M., N. Savoye, F. Dehairs, V.H. Strass, and D. Cardinal. 2008. Mesopelagic carbon reminer- alization during the European iron fertilization experiment. *Global Biogeochemical Cycles* 22, GB1023,

doi:10.1029/2006GB002902.

- Keeling, C.D. (1958). "The concentration and isotopic abundances of atmospheric carbon dioxide in rural areas." *Geochimica et Cosmochimica Acta, 3*(4): pp.322-334
- Keith D, M. Ha-Duong and J. Stolaroff (2006). "Climate Strategy with CO2 Capture from the Air." *Climate Change*, 74: 17–45.
- Kheshgi, H.S. (1995). "Sequestering atmospheric carbon dioxide by increasing ocean alkalinity." *Energy*, *20*(9): 915-922
- Kiehl, J.T. and K.E. Trenberth, 1997: Earth's Annual Global Mean Energy Budget, Bulletin of American Meteorological Society 78(2), 197-208.
- Klaas, C. and D.E. Archer (2002). "Association of sinking organic matter with various types of mineral ballast in the deep sea: Implications for the rain ratio." *Global Biogeochemical Cycles, 16*(4): 1116
- Köhler, P., J. Hartmann, and D.A. Wolf-Gladrow (2010). "The geoengineering potential of artificially enhanced silicate weathering of olivine." *Proceedings of the National Academy of Sciences of the United States of America, 107*(47): 20228-20233
- Lackner, K.S. (2002). "Carbonate chemistry for sequestering fossil carbon." *Annual Review of Energy and the Environment,* 27: 193–232.

Lackner, K.S. (2003). "A guide to CO2 sequestration." Science, 300: 1677–1678.

Large, W., J. McWilliams, and S. Doney (1994), Oceanic vertical mixing: A review and a model with nonlocal boundary layer parameterization, Rev. Geophys., 32, 363-403.

- Large, W.G. and S.G. Yeager (2008): The global climatology of an interannually varying air-sea flux data set. *Climate Dynamics* 33(2-3): 341-364, DOI 10.1007/s00382-008-0441-3
- Laruelle, G.G., V. Roubeix, A. Sferratore, B. Brodherr, D. Ciuffa, D.J. Conley, H.H. Dürr, J. Garnier, C. Lancelot, Q. Le Thi Phuong, J.-D. Meunier, M. Meybeck, P. Michalopoulos, B. Moriceau, S. Ní Longphuirt, S. Loucaides, L. Papush, M. Presti, O. Ragueneau, P. Regnier, L. Saccone, C.P. Slomp, C. Spiteri, and P. Van Cappellen (2009). "Anthropogenic perturbations of the silicon cycle at the global scale: Key role of the land-ocean transition." *Global Biogeochemical Cycles*, *23*(4): 1-17.
- Lenton T.M., H. Held, E. Kriegler, J.W. Hall, W. Lucht, S. Rahmstorf, and H.J. Schnullnhuber (2008). "Tipping elements in the Earth's climate system." *Proceedings of the National Academy of Science of the United States of America, 105*: 1786–1793.
- Lenton, T.M., and N.E. Vaughan (2009). "The radiative forcing potential of different climate geoengineering options." *Atmospheric Chemistry and Physics, 9*: 5539-5561.
- Lerman, A., D.D. Li, F.T. MacKenzie (2010). "Global Biogeochemical Cycle of Si: Its Coupling to the Perturbed C-N-P cycles in Industrial Time." *American Geophysical Union*, Fall Meeting 2010, abstract #B11D-0391
- Le Quéré, C., M.R. Raupach, J.G. Canadell, and G. Marland (2009). "Trends in the sources and sinks of carbon dioxide." *Nature Geoscience*, *2*(12): 831-836.
- Losch, M, M. Schroeder, S. Hohn, and C. Voelker (2008). "High-Resolution Modelling of Phytoplankton Distribution and Adaptation." NIC Symposium 2008. *NIC Series, 39*: 289-296
- Maritorena, S, and D.A. Siegel (2005): Consistent merging of satellite ocean color data sets using a bio-optical model. *Remote Sensing of the Environment*, 94(4): 429-440

- Marshall, J., A. Adcroft, C. Hill, L. Perelmen, and C. Heisey (1997). "A finite-volume, incompressible Navier Stokes model for studies of the ocean on parallel computers." *Journal of Geophysical Research, 102*: 5753-5766.
- Matter, J.M., and P.B. Kelemen (2009). "Permanent storage of carbon dioxide in geological reservoirs by mineral carbonation." *Nature Geoscience, 2*(12): 837–841.
- Matthews, B. Photo. nature.com last viewed: 14 June, 2011. http://www.nature.com/nature/journal/v409/n6818/images/409420aa.2.jpg>
- McNeil, B.I., N. Metzl, R.M. Key, R.J. Matear, and A. Corbiere (2007). "An empirical estimate of the Southern Ocean air-sea CO2 flux." *Global Biogeochemical Cycles, 21*, GB3011
- Meinshausen M., N. Meinshausen, W. Hare, S.C.B Raper, K. Frieler, R. Knutti, D.J. Frame, and M.R. Allen (2009). "Greenhouse-gas emission targets for limiting global warming to 2∘C." *Nature, 458*: 1158–1162.
- Mikaloff Fletcher, S. E., N. Gruber, A.R. Jacobson, M. Gloor, S.C. Doner, S. Dutkiewicz, M. Gerber, M. Follows, F. Joos, K. Lindsay, D. Menemenlis, A. Mouchet, S.A. Muller, and J.L. Sarmiento (2007). "Inverse estimates of the oceanic sources and sinks of natural CO2 and the implied oceanic transport." *Global Biogeochemical Cycles, 21*, GB1010.
- MITgcm Group (2002). MITgcm Release 1 Manual, Online documentation, MIT/EAPS, Cambridge, MA 02139, USA, 2002, http://mitgcm.org/sealion/online documents/manual.html.
- Nelson, D.M., P. Treguer, M.A. Brzezinkski, A. Laynaert, and B. Queguiner (1995).
 "Production and Dissolution of Biogenic Silica in the Ocean: Revised Global Estimates, Comparison With Regional Data and Relationship to Biogenic Sedimentation." *Global Biogeochemical Cycles*, 9(3): 359–372.

- NOAA. Photo. esrl.noaa.gov last viewed: 19 January, 2011. http://www.esrl.noaa.gov/gmd/webdata/ccgg/trends/co2_data_mlo.png>
- Olson, E. (2006). Oceanic Transports of Heat and Salt from a Global Model and Data. Master's Thesis: The Massachusetts Institute of Technology September 2006
- Passow, U. (2002). Transparent exopolymer particles (TEP) in aquatic environments. *Progress in Oceanography, 55*: 287–333.
- Ragueneau, O., P. Treguer, A. Leynaert, R.F. Anderson, M.A. Brzezinski, D.J. DeMaster, R.C. Dugdale, J. Dymond, G. Fischer, R. Francois, C. Heinze, E. Maier-Reimer, V. Martin-Jezequel, D.M. Nelson, and B. Queguiner (2000). "A review of the Si cycle in the modern ocean: recent progress and missing gaps in the application of biogenic opal as a paleoproductivity proxy." *Global and Planetary Change*, *26*(4): 317 365.
- Ragueneau, O., S. Schultes, K. Bidle, P. Claquin, and B. Moriceau (2006). "Si and C interactions in the world ocean: importance of ecological processes and implications for the role of diatoms in the biological pump." *Global Biogeochemical Cycles, 20*(4): 1-15.
- Raynaud, D., J. Jouzel, J.M. Barnola, J. Chappelaz, R.J. Delmas, and C. Lorius (1993). "The ice record of greenhouse gases." *Science*, *259*:26–934.
- Redfield, A.C., B.H. Ketchum, and F.A. Richards (1963). The influence of organisms on the composition of sea water, in: The Sea, edited by Hall, M. N., vol. 2, pp. 26–77, Wiley-Interscience, New York, 1963.
- Ridgwell, A., A. Watson, and D. Archer (2002). "Modeling the response of the oceanic Si inventory to perturbation and consequences for atmospheric CO2." *Global Biogeochemical Cycles, 16*(4).

- Riebesell U., V.J. Fabry, L. Hansson, and J.-P. Gattuso (Eds.) (2010). Guide to best practices for ocean acidification research and data reporting, 260 p. Luxembourg: Publications Office of the European Union.
- Ruddiman, W.F. (2001). Earth's climate: past and future. New York: W. H. Freeman and Company.
- Sabine, C.L., R.A. Feely, N. Gruber, R.M. Key, K. Lee, J.L. Bullister, R. Wanninkhof, C.S. Wong, D.W.R. Wallace, B. Tilbrook, F.J. Millero, T.-H. Peng, A. Kozyr, T. Ono, and A.F. Rios (2004). "The oceanic sink for anthropogenic CO2." *Science*, 305: 367 371.
- Sarmiento, J.L., and N. Gruber (2002). "Sinks for Anthropogenic Carbon." *Physics Today*, *55*: 30–36.
- Sarmiento, J.L. and Gruber, N. (2006): Ocean Biogeochemical Dynamics, Princeton University Press, Princeton, New Jersey, 2006.
- Schartau, M., A. Engel, J. Schroeter, S. Thoms, C. Voelker, and D.A. Wolf-Gladrow (2007). "Modelling carbon overconsumption and the formation of extracellular particulate organic carbon." Biogeosciences, 4: 433–454
- Schimel, D.S. (1995). "Terrestrial ecosystems and the carbon cycle." Global Change Biology, 1(1): 77–91.
- Schneider, B., L. Bopp, M. Gehlen, J. Segschneider, T.L. Frolicher, P. Cadule, P. Friedlingstein, S.C. Doney, M.J. Gehrenfeld, and F. Joos (2008). "Climate-induced interannual variability of marine primary and export production in three global coupled climate carbon cycle models." Biogeosciences, 5: 597-614.
- Schuiling, R.D. and P. Krijgsman (2006) "Enhanced weathering: an effective and cheap tool to sequester CO2." *Climate Change*, 74: 349–354.

Seifritz, W. (1990). "CO2 disposal by means of silicates." Nature, 345(6275): 486.

- Siegenthaler, U., and J. Sarmiento (1993). "Atmospheric carbon dioxide and the ocean." *Nature*, *365*(6442): 119–125.
- Simmon, R. NASA Earth Observatory. Photo. prasoondiwakar.com published: 13 January, 2011. last viewed: 10 April, 2011. http://prasoondiwakar.com/wordpress/tag/climate/
- Smith J.B., S.H. Schneider, M. Oppenheimer, G.W. Yohe, W. Hare, M.D. Mastrandrea, A. Patwardhan, I. Burton, J. Corfee-Morlot, C.H.D. Magadza, H.-M. Fussel, A.B. Pittock, A. Rahman, A. Suarez, and J.-P. van Ypersele (2009). "Assessing dangerous climate change through an update of the Intergovernmental Panel on Climate Change (IPCC) reasons for concern." *Proceedings of the National Academy of Science of the United States of America, 106*: 4133–4137.
- Solomon S., G.K. Plattner, R. Knutti and P. Friedlingstein (2009). "Irreversible climate change due to carbon dioxide emissions." *Proceedings of the National Academy of Science of the United States of America, 106*: 1704–1709.
- Stammer, D., C. Wunsch, R. Giering, C. Eckert, P. Heimbach, J. Marotzke, A. Adcroft, C.N. Hill, and J. Marshall. (2003). Volume, heat, and freshwater transports of the global ocean circulation 1993-2000, estimated from a general circulation model constrained by World Ocean Circulation Experiment (WOCE) data. *Journal of Geophysics Research, 108*: 3007.
- Stephens J. and D. Keith (2008). "Assessing geochemical carbon management." *Climate Change*, 90: 217–242.
- Steen, B. and G. Borg (2002) An estimate of the cost of sustainable production of metal concentrates from the Earth's crust. *Ecological Economics*, 42(3): 401-413.
- Stott, L.D. Photo. earth.usc.edu last viewed: 27 May, 2011. http://earth.usc.edu/classes/geol150/stott/variability/co2.html

- Stow, A.C., J. Jolliff, D.J. McGillicuddy Jr., S.C. Doney, J.I. Allen, M.A.M. Friedrichs, K.A. Rose and P. Wallhead (2009). Skill assessment for coupled biological/physical models of marine systems. *Journal of Marine Systems*, 76(1-2): 4-15
- Strong, A.L., J.J. Cullen, and S.W. Chisholm (2009). "Ocean Fertilization: Science, Policy, and Commerce." *Oceanography*, *22*(3): 236-261
- Takahashi, T. S.C. Sutherland, C. Sweeney, A. Poisson, N. Metzi, B. Tillbrook, N. Bates, R. Wanninkhof, R.A. Feely, C. Sabine, J. Olafsson, and Y. Nojiri (2002). "Global sea–air CO2 flux based on climatological surface ocean pCO2, and seasonal biological and temperature effects." *Deep Sea Research Part II: Topical Studies in Oceanography, 49*(9-10): 1601-1622.
- Takahashi, T., S.C. Sutherland, R. Wanninkhof, C. Sweeney, R.A. Feely, D.W. Chipman, B. Hales, G. Friederich, F. Chavez, C. Sabine, A. Watson, D.C.E. Bakker, U. Schuster, N. Metzi, H. Yoshikawa-Inoue, M. Ishii, T. Midorikawa, Y. Nojiri, A. Kortzinger, T. Steinhoff, M. Hoppema, J. Olafsson, T.S. Arnarson, B. Tilbrook, T. Johannessen, A. Olsen, R. Bellerby, C.S. Wong, B. Delille, N.R. Bates, and H.J.W. de Baar (2009). "Climatological mean and decadal change in surface ocean pCO2 and net sea-air CO2 flux over the global oceans." *Deep Sea Research Part II: Tropical Studies in Oceanography, 56*: 554 577.
- The Royal Society (2009). Geoengineering the climate: Science, governance, and uncertainty. London: Techset Composition Limited.
- Treguer, P., D.M. Nelson, A.J. Van Bennekom, D.J. DeMaster, A. leynaert, and B. Queguiner (1995). "The Silica Balance in the World Ocean: A Reestimate." *Science*, *268*(5209): 375–379.
- Tsuda, A., H. Kiyosawa, A. Kuwata, M. Mochizuki, N. Shiga, H. Saito, S. Chiba, K. Imai, J. Nishioka, and T. Ono (2005). "Responses of diatoms to iron-

enrichment (SEEDS) in the western subarctic Pacific, temporal and spatial comparisons." *Progress In Oceanography* 64(2-4): 189-205

- United Nations (1998). "Kyoto Protocol to the United Nations Framework Convention on Climate Change."
- University of Maryland. Photo. bbc.co.uk published: 10 March, 2009. last viewed: 5 May, 2011. http://news.bbc.co.uk/2/hi/science/nature/7933589.stm
- Wallace, J.M. and P.V. Hobbs (2006). Atmospheric Science: An Introductory Survey (2nd Ed.). Academic Press Publications

Wayne, R.P. (2000). Chemistry of Atmospheres (3rd Ed.). Oxford University Press.

- Weller, R. Cochise Collge. Photo. published: 2010. last viewed: 12 January, 2011. http://skywalker.cochise.edu/wellerr/mineral/olivine/olivineL.htm
- Wells, M.L. (2003). "The level of iron enrichment required to initiate diatom blooms in HNLC waters." *Marine Chemistry*, 82(1–2): 101–114.
- Zaihua Liu, Z., W. Dreybrodt, and H. Liu (2011). "Atmospheric CO2 sink: Silicate weathering or carbonate weathering?" *Applied Geochemistry* 26: S292–S294
- Zanette, D.H. Photo. wikipedia.com published: 16 July 2008. last viewed: 13 June, 2011. <http://en.wikipedia.org/wiki/File:Diatomeas_w.jpg>
- Zeebe, R.E. and D.A. Wolf-Gladrow (2001). CO2 in Seawater: Equilibrium, Kinetics, Isotopes, vol. 65 of Elsevier Oceanography Book Series, Elsevier Science Publishing, Amsterdam, The Netherlands, 2001.
- Zeebe, R.E., and C. Archer (2005). "Feasibility of ocean fertilization and its impact on future atmospheric CO2 levels." *Geophysical Research Letters*, 32(9): 1-5.