
THE EFFECT OF OCEAN ACIDIFICATION ON CALCIFYING FORAMINIFERA

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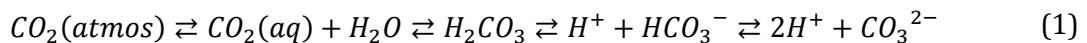
ABSTRACT

Ocean acidification is the anthropogenic change in ocean chemistry driven by the oceanic uptake of chemical inputs in the atmosphere, most importantly that of CO_2 . The increase of CO_2 in the ocean causes the acidity of the ocean to increase, causing the production of calcium carbonate (CaCO_3) to decrease. Foraminifera are a group of protists that are often protected by a calcite test, and therefore may be hindered by the increasing acidity of the ocean. In this review article I discuss the process of ocean acidification, the adaptations of Foraminifera to low pH conditions and the reaction of Foraminifera to the ongoing ocean acidification. I used the four Representative Concentration Pathways to assess possible future situations. I conclude that compared to other calcifying organisms Foraminifera are likely to survive the ongoing ocean acidification, because they have evolved different strategies to keep their calcite production up. They also produce a form of calcium carbonate that is capable of surviving lower acidities than many other organisms, both in structure and in Magnesium content.

INTRODUCTION

OCEAN ACIDIFICATION

With the use of fossil fuels and global deforestation that started in the Industrial revolution, the CO₂ levels in the atmosphere around the world have increased by about 40% (Solomon et al, 2007). This has had many effects, the most obvious being the increase in air temperature (global warming). However, since the atmospheric CO₂ is in equilibrium with the CO₂ concentration in the oceans, the CO₂ concentration in the oceans is also rapidly increasing, causing another problem. A large portion of the CO₂ emission is taken up by the sea:



The equilibrium between the CO₂ concentration in the atmosphere and the Dissolved Inorganic Carbon (DIC, the sum of the CO₂ (aq), H₂CO₃, HCO₃⁻ and CO₃²⁻) in seawater is established in approximately one year (Doney et al, 2009). At the current ocean acidity, the DIC in the ocean is usually present in the form of HCO₃⁻ + H⁺ (Figure 1). This extra Hydrogen ion is a major contributor to ocean acidification. Ocean acidification may be defined as the change in ocean chemistry driven by the oceanic uptake of chemical inputs to the atmosphere, including carbon, nitrogen, and sulfur compounds (Guinotte & Fabry, 2008). In most areas, the carbon compounds are the biggest contributors to ocean acidification, since Nitrogen and Sulphur compounds are often short-lived and are therefore deposited mostly on land (Doney et al, 2007).

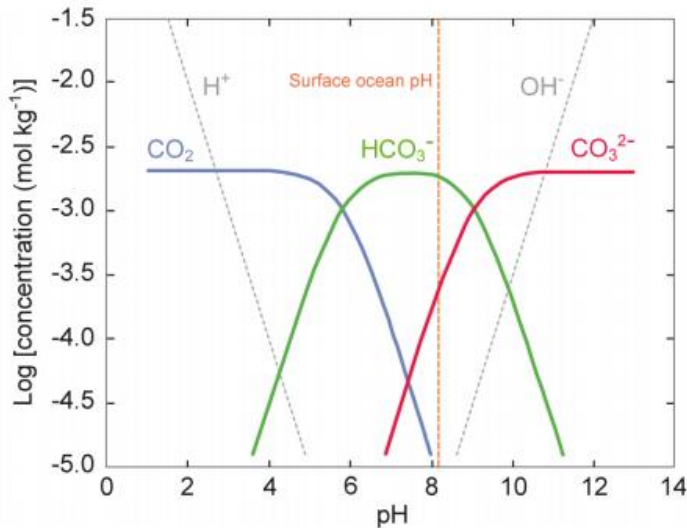


Figure 1. The Bjerrum plot, showing the form in which DIC is present in the ocean at different acidities. The dashed vertical line represents the current ocean acidity (Source: <http://www.nature.com/scitable/knowledge/library/ocean-acidification-25822734>).

The current speed of this process is about 0.02 pH per decade (Royal Society, 2005). The acidity before the Industrial revolution was around 8.21 and has so far decreased to 8.10 (Royal Society, 2005). It is expected to decrease at least another 0.3-0.4 pH with the current CO₂ increase (Orr et al, 2005). Since the pH is the $-\log_{10}[\text{H}^+]$, the concentration of hydrogen ions in seawater will increase with a factor $10^{0.3}-10^{0.4} = 2-2.5$.

FORAMINIFERA

Foraminifera or forams are one of the most numerous and widespread groups of marine protists. As of 2014, 8380 extant species have been recognized (World Foraminifera Database). Most species have a calcareous outer shell, although some naked species exist in fresh water (Pawlowski et al, 1999) and some species use an organic-walled shell (Gooday et al, 2008). The organisms consist of only one cell, but most are colonial and may appear multicellular. Both benthic and planktonic species exist, and both can be found throughout the world's oceans.

Because of the abundance of Foraminifera, they play an important role in the global marine ecosystems. Most species are classed as small heterotrophes, and feed on phytoplankton; however, some species have unicellular algae as endosymbionts which are able to perform photosynthesis (Bernhard & Bowser, 1999). Many animals live mostly on foraminifera, for example sand dollars, marine snails and small fish, some of which have a diet that consists almost solely of foraminifera.

The foraminiferal fixing of calcium carbonate amounts to 25% of the total calcium carbonate production in the oceans (Langer, 2008). The sinking of dead pelagic Foraminifera species is one of the big downward particle fluxes in the open ocean: it is estimated to be about 12% of the total downward particle flux (Silver & Gowing, 1991). Therefore, foraminifera are critical in the ocean chemistry.

The first fossil records of test-bearing Foraminifera were found in Cambrian sediments (Culver, 1991), and it is believed that the first naked Foraminifera have evolved in the late Proterozoic (Wray et al, 1994; Pawlowski et al, 2003). Nowadays benthic foraminifera can be found in almost all marine areas, from the intertidal to the deep ocean and from fresh water to the Dead Sea (Pawlowski et al, 1999; AlmolgiLabin et al, 1995; Gooday et al, 2008; Bergsten, 1994). Planktonic foraminifera live mostly in the top 100 to 200 meter (Mortyn & Charles, 2003). Although most species are aquatic, one terrestrial species has even been found in a tropical rainforest, living in the soil (Meisterfeld et al, 2001).

Together with other protists with a calcareous or siliceous exoskeleton, Foraminifera are often used as a key group for identifying fossil sediments. Because of their small size, microfossils are often better preserved than macrofossils: especially foraminifera can be found in the most eroded sediment layers. The most important information that can be derived from fossil foraminifera in these layers is the ocean temperature at the time of fossilization (Nürnberg et al, 1995). By measuring the Mg^{2+}/Ca^{2+} ratio in the calcite of their exoskeleton and looking at the species composition the temperature at which the calcite was fixed can be calculated with decent accuracy (Nürnberg et al, 1995).

Furthermore, the Foraminiferal species composition can be used to estimate the age of a fossil layer without the use of radiometric dating methods. The evolution of the important groups of test-bearing foraminifera is well known, and the presence, absence and dominance of species groups (which can be determined by using an electronic or light microscope) is often enough to identify the fossil layer.

The information about sediments is also used to locate fossil fuels. In the 1980's, the expert system Vides (Visual Identification Expert System) was developed by the oil company BP (Athersuch et al, 1994). It allows the user to identify possible petroleum sources by visual examination of the microfossils in the area.

Foraminifera that use a calcareous outer test produce this test by fixating the Ca^{2+} ion that is abundant in the ocean. However, in fixating this ion, it is dependent on many physical conditions,

most notably the pressure (or depth) and the acidity. In this thesis I will explore the effects of ocean acidification on Foraminifera using the latest climate models and knowledge of Foraminifera, and explore the potential effects of the disappearing of the group on the Benthic ecosystem. Although this paper focuses on acidification, not on global warming, I explicitly take global warming into account where possible because the effects of CO₂ and temperature are intertwined and it would be unrealistic to regard one aspect of climate change in isolation, ignoring the other one.

METHODS

This thesis is based upon a literature review. Articles used in this review paper have been found by using the online search catalogues Web of Science and Google Scholar. In total around 80 articles on ocean acidification, the calcifying process and foraminifera have been examined, most of which from the last decade. The Citation Map option in Web of Science was used to find related articles, both the forward and backward function. Some books on Foraminifera and climate change were used for general information on the subject. I have also used the Fifth assessment of the IPCC for the present state of the changing climate.

Search terms that have been used to find articles on the subject include “Foraminifera + Ocean Acidification”, “Calcification + Foraminifera” and “global warming + calcification”.

THE PROCESS OF OCEAN ACIDIFICATION AND ITS EFFECT ON FORAMINIFERA

The fixation of Calcium by marine organisms is dependent on the acidity of the ocean. When the ocean acidity increases (pH decreases), organisms will have trouble fixing Calcium. Foraminifera depend on Calcium fixation for their growth, and experiments show that their growth will be inhibited with a increasing acidity (Haynert et al, 2014; Dias et al, 2010). Some experiments even suggest that with the current increase in atmospheric CO₂, many calcifying organisms including Foraminifera may be unable to survive the next 100 years because of Calcium deficiency (Orr et al, 2005). Since Foraminifera produce about 1.4 billion tons of calcium carbonate per year, they are one of the biggest calcium carbonate producers in the ocean: it is estimated that they produce almost 25% of the total calcium carbonate production in the ocean (Langer, 2008). Therefore, their disappearance would have significant effects on the chemistry of the world's oceans.

In seawater, calcium is usually present either as a loose ion Ca²⁺ or as calcium carbonate CaCO₃. These two forms are at an equilibrium (after Doney et al, 2009):



The saturation state (Ω) varies with the ionic calcium and carbonate concentrations (after Doney et al, 2009):

$$\Omega = [Ca^{2+}][CO_3^{2-}]/K'_{sp} \quad (3)$$

Where the solubility product K'_{sp} depends on the conditions, most importantly on the temperature, salinity and pressure. When $\Omega < 1$ the CaCO₃ will dissolve, and when $\Omega > 1$ CaCO₃ can be produced.

The possibility to produce calcium carbonate also depends on the form in which it crystallizes. In the ocean calcium carbonate is produced in two different ways, resulting in two different crystal structures: Aragonite (produced by reef-building corals and some molluscs) and calcite (produced by Foraminifera, Coccolithophores and some molluscs). Of the two, aragonite generally has a lower K'_{sp} value and is therefore more likely to get a value of $\Omega < 1$, the threshold for dissolving.

The $[Ca^{2+}]$ is usually proportional to the salinity and is therefore not likely to change much (Doney et al, 2009). The $[CO_3^{2-}]$, however, is decreasing with the increase of atmospheric CO_2 concentrations, resulting in a decreased Ω and therefore an increased dissolution rate of $CaCO_3$ (Fig. 2). Since the K'_{sp} decreases with pressure, the formation of both calcite and aragonite is usually limited to a certain depth; this depth decreases with an increase in the atmospheric CO_2 concentration. Therefore, deep water species are predicted to go extinct first because they are unable to fix Calcium and upkeep their shell (Fig. 3).

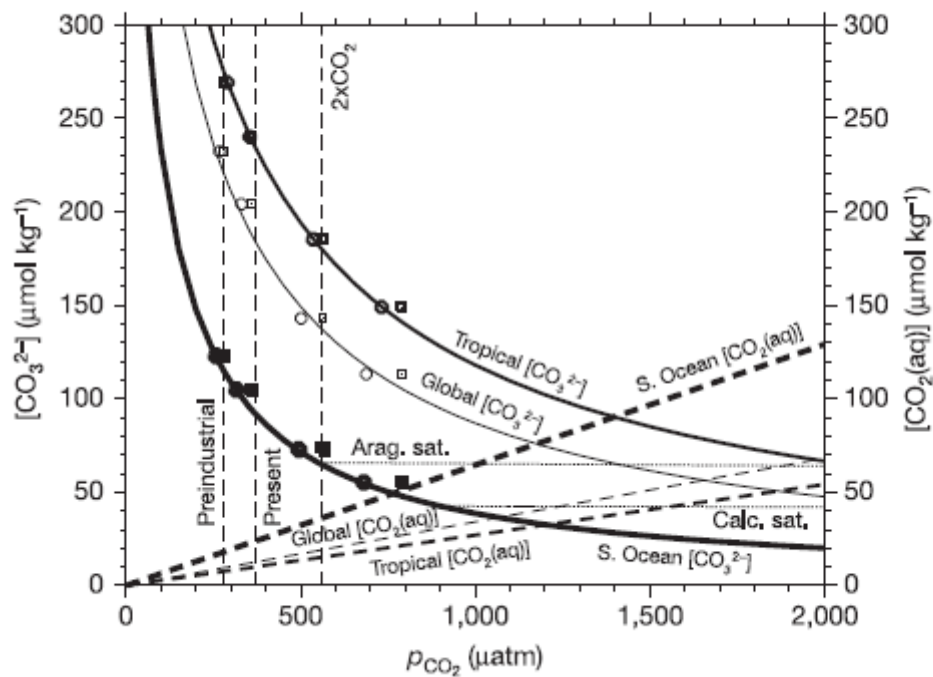


Figure 2. The solid lines show the CO_3^{2-} concentrations at the surface for different atmospheric CO_2 concentrations for global, tropical and Southern ocean seawater at different atmospheric CO_2 pressure. The dashed lines show the equilibrium between atmospheric and dissolved CO_2 for the global, tropical and Southern ocean seawater. The vertical dotted lines represent the preindustrial (~ 1830), present (2005) and double industrial CO_2 concentrations. The horizontal dotted lines are the aragonite and calcite equilibrium lines. The vertical distance from a point on the solid line to the calcite equilibrium line is an indication for the effort needed to create calcite. From Orr et al, 2005.

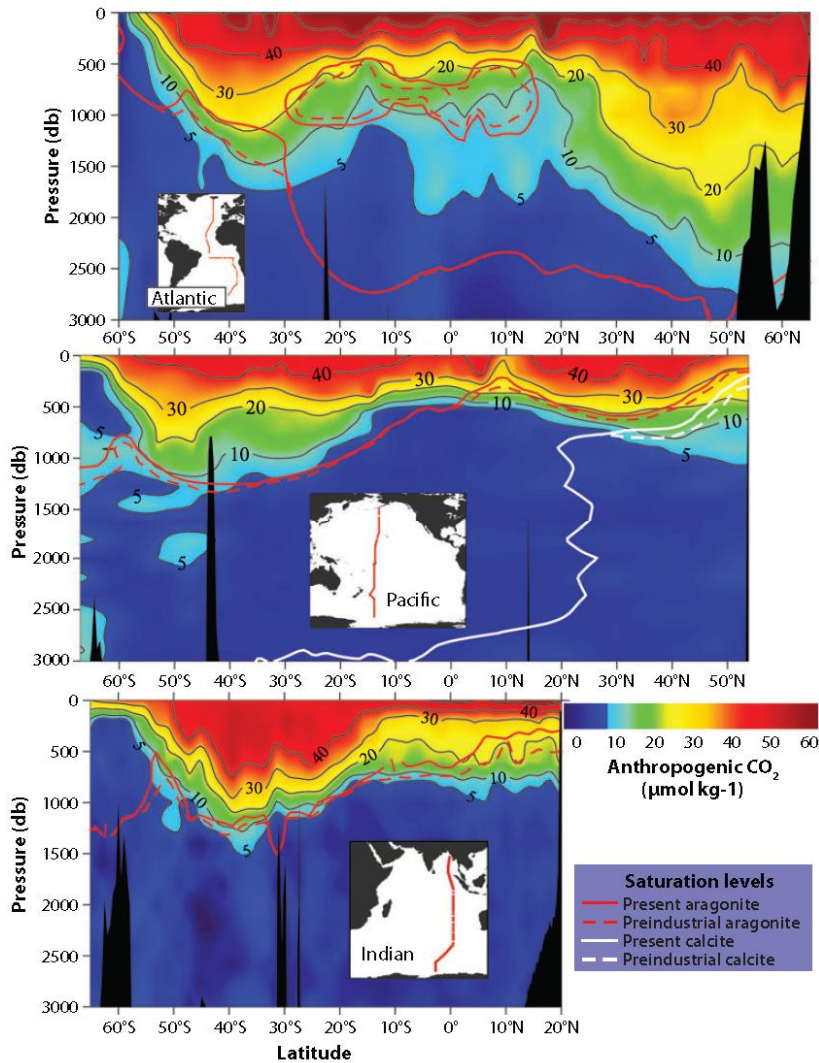


Figure 3. The equilibrium lines (=1) for Argonite (red) and calcite (white) in the three major oceans, on a South-North traject for the Atlantic, Pacific and Indian ocean. Dotted line represents the preindustrial equilibrium line, the solid line the present state. Colors indicate the current anthropogenic CO₂ concentrations. Pressure (db) is an indicator for depth, with 1 bar ≈ 10 m. From Doney et al, 2009.

In the evolution of the calcium carbonate skeleton the advantages of the different pathways depended on the Magnesium and Calcium concentrations in the ocean: periods with relatively high Ca²⁺ concentrations and low Mg²⁺ concentrations have favored organisms that produced calcite, while low Ca²⁺ concentrations and high Mg²⁺ concentrations favored organisms that produced aragonite (Wilkinson, 1979). However, with the rapidly changing acidity of the ocean, calcite producers like Foraminifera might hold an advantage over aragonite producers again.

ADAPTATIONS FOR INCREASING THE SATURATION STATE

Over the course of evolution, many Foraminifera groups and species have evolved specific mechanisms that enable them to survive lower ambient acidities and increase their calcite production. In this regard test-bearing Foraminifera can be classified into two paraphyletic, morphological groups (Pawlowski et al, 2013): Miliolid and Hyaline Foraminifera. Miliolids form

needles of calcite, giving a porous surface, while Hyaline Foraminifera produce a porcelaneous test.

ACTIVELY DECREASING Mg^{2+} CONCENTRATIONS

The Magnesium ion Mg^{2+} is an important inhibitor for calcite production for two reasons. Firstly, the total activity coefficient of CO_3^{2-} is reduced in the presence of Mg^{2+} , since CO_3^{2-} and Mg^{2+} form relatively strong ionic bonds in seawater (Zeebe & Sanyal, 2001). This decreases the amount of “free” CO_2 in a solution, on which the production of $CaCO_3$ depends.

Secondly and most importantly (Zeebe & Sanyal, 2001), the fixation of $CaCO_3$ will incorporate some $MgCO_3$ in the crystal structure, because the two molecules have similar structures. This crystal structure with both Calcium carbonate and Magnesium carbonate is much less stable than a crystal structure with only calcium carbonate. Because this effect is so strong, many calcifying organisms including all hyaline Foraminifera and coccolithophorid actively exclude Mg^{2+} from their cytoplasm (Wilkinson, 1979; Zeebe & Sanyal, 2001; Ries, 2005). Since membranes are usually impermeable to ions, a low Mg/Ca ratio can be upheld to allow the production of calcite structures almost without magnesium. All planktonic and some benthic Foraminifera have a low Mg/Ca concentration. The mechanism with which Magnesium is excluded from the cell has not yet been demonstrated.

The pH required for calcite production also shows a clear inhibition effect of Mg^{2+} . An experimental study performed by Zeebe and Sanyal (2001) demonstrated that at low pressures with a Mg^{2+} concentration of 53 mmol kg^{-1} a pH of 9.9 is required, while in the absence of Magnesium a pH of 8.2 is required for calcification (Fig. 4). The pH that is required for calcite production when the seawater is depleted of Mg^{2+} is approximately the pH of seawater; therefore, the removal of all Mg^{2+} from the cell is a potential way of producing calcite.

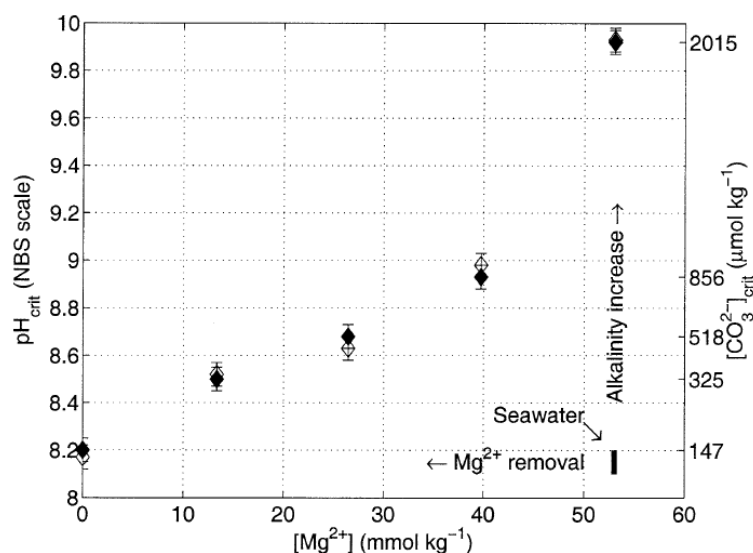


Figure 4. The critical pH values for different Mg^{2+} concentrations, defined as the pH at which calcite precipitation could be measured. The different diamonds represent the duplo measurements. The required CO_3^{2-} concentrations for calcite precipitation are approximately 13 times higher for a Mg^{2+} concentration of 53 mmol kg^{-1} than for Mg^{2+} depleted seawater. From Zeebe & Sanyal, 2001.

ALTERING THE ACIDITY IN THE CELL

An alternative approach for increasing the calcite precipitation in the cell is increasing the intracellular pH. De Nooijer et al. (2009) showed that both Miliolid and Hyaline Foraminifera actively remove protons from the cytoplasm to elevate their pH. In this experiment, the pH of living Foraminifera was visualized using a ratiometric fluorescent probe, and it demonstrated how Foraminifera from different groups are able to perform calcification even under high Mg/Ca conditions.

Removing protons from the cell has advantages and disadvantages when compared to the removal of magnesium. The most important advantage is that for an elevation of the pH from 8.0 to 10.0 only approximately $3 \text{ mmol kg}^{-1} \text{ H}^+$ ions have to be removed, compared to the removal of 53 mmol Mg^{2+} (the concentration in seawater). Assuming that the transport of one Mg^{2+} ion costs approximately twice as much as the transport of one H^+ ion because of the doubled ionic charge (Zeebe & Sanyal, 2001), the cost of reaching the saturation level by increasing the pH is about $53/3=35$ times less than by removing the Mg^{2+} . However, the cellular membrane is permeable to neutral atoms like H_2O and CO_2 , and the addition of CO_2 to a medium with a high acidity will cause it to react with water to form calcite and two protons (Equation 1). Therefore the removal of protons is a continuous process.

PREDICTIONS OF THE LATEST CLIMATE MODELS

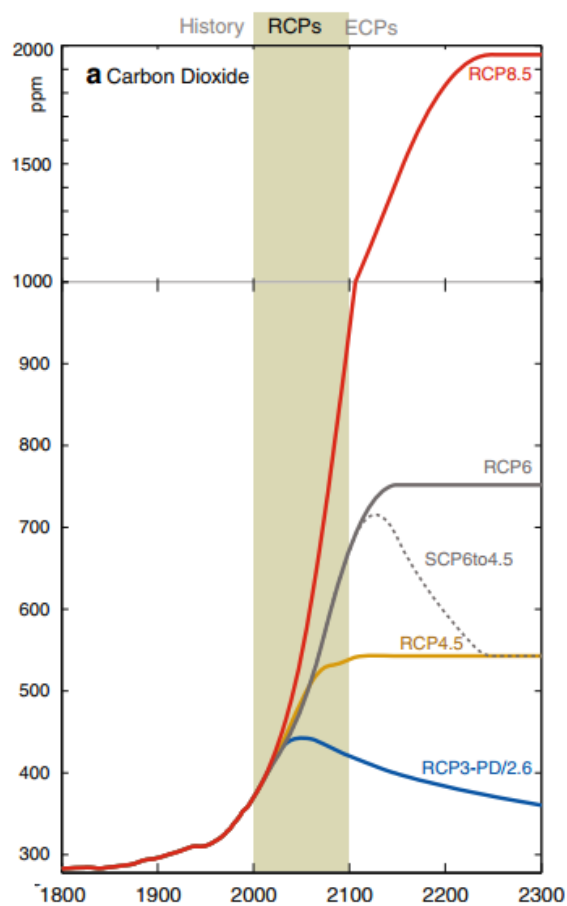


Figure 5. The predicted atmospheric CO_2 over the next 3000 years according to the four Representative Concentration Pathways, the RCP8.5, RCP6, RCP4.5 and RCP2.6. The grey bar represents the 21st century. The red line before 2010 is based on atmospheric measurements. From Meinshausen et al, 2011.

In 2013, the Intergovernmental Panel on Climate Change (IPCC) released the fifth assessment report on climate change under the title *Climate Change: The Physical science basis* (Stocker et al, 2013). The previous climate report brought out by the IPCC was released in 2007. Here I will discuss the conclusions from the fifth assessment that are important to the topic of this paper. Note that as of June 2014 the atmospheric CO_2 concentration is 401.30 ppm (CO2now.org) and the radiative forcing value is 2.916 W m^{-2} (Collins et al, 2013).

In this report, multiple Representative Concentration Pathways or RCP's are used, based on the possible near-future anthropogenic and natural gas emissions. Four RCP models were developed (Moss et al, 2010), the RCP2.6, RCP4.5, RCP6.0, and RCP8.5 model; these are named after the expected radiative forcing values or energy absorbed by the earth's atmosphere by 2100 in W m^{-2} (the current radiation is around 3.0 W m^{-2}). To model the climate scenarios after 2100 the Extended Concentration Pathways or ECP's are often used; these follow the four RCP models. I will briefly go over each of the RCP models and the consequences on the chemical composition of the ocean.

In the RCP 2.6 model, proposed by the Netherlands Environmental Assessment Agency, the global CO₂ emission reaches its peak within the next two decades (Moss et al, 2010; after Van Vuuren et al, 2007). It is the most optimistic of the models, because with the rapid increase in CO₂ emission a decrease within two decades is unlikely. However, if anthropogenic CO₂ emission decreases within this time frame, a decrease in atmospheric CO₂ is possible, and an equilibrium atmospheric CO₂ concentration of 350 parts per million is predicted – which is about the same as present CO₂ concentration. The deep water ocean acidity will still increase for hundreds of years, since the current equilibrium between atmospheric CO₂ and ocean DIC has not yet reached the deep ocean.

In the RCP 4.5 model, the global CO₂ emission reaches its peak around 2040 because of technological improvements that allow for a reduction in the emission of greenhouse gases (RCP database). The atmospheric CO₂ concentration will reach an equilibrium at around 550 ppm in 2100. This model is considered to be more likely than the RCP 2.6 model. However, since in 66% of the world's countries the CO₂ emission is still growing (world bank group), a lot has to change before this model will be the most accurate. However, if this model proves to be correct, Foraminifera would probably be okay since even in the Southern Ocean the CO₂ levels will get nowhere near the calcite equilibrium line (fig. 3).

The RCP 6.0 model is a stabilization scenario where the CO₂ emission is stabilized after 2100 but will eventually reach an equilibrium by employment of a range of technologies and strategies for reducing greenhouse gas emissions (RCP database). The atmospheric CO₂ concentration will stabilize at around 750 ppm (Meinshausen et al, 2011; fig. 4). In the Southern ocean this may cause problems for the calcifying Foraminifera; the process of calcifying will be much more difficult since the availability of CO₃²⁻ will go down rapidly.

The latest and most severe model, the RCP 8.5 model, is the model in which the anthropogenic CO₂ emission keeps increasing with the rate at which it is increasing now (Moss et al, 2010). The CO₂ emission does not reach a peak before 2100 and instead will increase by a factor 4 between 2000 and 2100 (RCP database). This model is sometimes regarded as impossible, since the amount of fossil fuels could not support this amount of emission. It is, however, the direction in which we are going currently with “business as usual” and no drastic mitigation measures.

This model predicts an increase to around 2000 ppm by 2300 (Meinshausen et al, 2011). As a result, the equilibrium line where calcite will dissolve spontaneously will reach the surface in most areas of the world, except for the tropics (Figure 3): for example, the dissolved CO₃²⁻ concentration in the Southern Ocean at 2000 ppm atmospheric CO₂ is about 30 μmol kg⁻¹, while the equilibrium line is at around 50 μmol kg⁻¹. This means that most test-bearing foraminifera around the world will disappear.

CONCLUSIONS & DISCUSSION

The performance of Foraminifera is dependent on the concentrations of Ca²⁺ and CO₃²⁻ and on the Solubility product K_{sp} (Equation 3); the higher the solubility product, the easier it is for Foraminifera to bind Ca²⁺ and produce calcite. The value of K_{sp} , however, is not constant, and is dependent on the physical conditions, most importantly the temperature, acidity and pressure (see “The process of ocean acidification and its effect on Foraminifera”). The increasing acidity of the ocean that is occurring presently is decreasing the available CO₃²⁻ in the ocean. The spontaneous reaction of Ca²⁺ and CO₃²⁻ is also inhibited by other chemicals in the ocean, among

which the Magnesium ion Mg^{2+} . The DIC concentrations at the surface can be predicted, because these concentrations follow the CO_2 concentrations in the atmosphere (Doney et al, 2009).

We do not know what climate model or scenario will prove to be the most accurate for predicting the future CO_2 emissions, but we see that three out of four IPCC scenarios show a significant increase in the next century. Since the performance of foraminifera is dependent on the depth, temperature and future CO_2 levels there will always be a threshold below which foraminifera are unable to maintain a calcite skeleton, and the depth of that line will depend on the future atmospheric CO_2 content. Planktonic foraminifera only inhabit the top 100-200 meter of the ocean and therefore will be affected by an increasing pH later than benthic foraminifera.

The RCP climate models that have been used in this thesis allow us to predict the future CO_2 levels, and the measurements by Orr et al. (2005; Fig. 3) allow us to look at the changing availability of CO_3^{2-} that will follow this CO_2 concentration. Since the difficulty to produce calcite is dependent on the carbonate concentration (Equation 3) and the carbonate concentration is negatively correlated with the atmospheric CO_2 concentration, we can conclude that an increasing atmospheric CO_2 concentration will decrease the production of calcite, and thus affect foraminifera, even if the equilibrium line of $\Omega=1$ is never reached.

The RCP 2.6 and RCP 8.5 models can be considered the extreme future scenarios; the RCP 2.6 scenario assumes a decrease in CO_2 emission from 2030 and the RCP 8.5 model assumes a steady increase in which policy makers don't intervene: assuming this model is the most accurate for a while, then the adverse effects of climate change should encourage people to search for alternatives. Since the RCP models are not modeled from a socio-economical perspective (Collins et al, 2013) it is hard to conclude from them what feedback the ongoing climate change will have on the anthropogenic emission of greenhouse gases such as CO_2 .

So, concluding that foraminifera will indeed be significantly affected by ocean acidification, can we expect major impacts on our marine ecosystems, and marine foodwebs? Since foraminifera are food to many organisms where they are abundant, their disappearance might result in the disappearance of specific heterotrophes. The benthic foraminifera are often food to benthic filter feeders e.g. benthic fish, sea snails and buried sea urchins, which might decrease with the disappearance of benthic foraminifera. Alternative food for these animals could be diatoms and ciliates; since these groups have a siliceous exoskeleton they will not be affected by the increasing ocean acidity. So based upon the evidence available, I don't expect any major impacts on food webs.

Planktonic foraminifera occur throughout the warmer oceans, but they are often present in smaller densities. As far as I could find, there are no species for which foraminifera are a large part of their diet. Since there is no competition for either carbonate or ionic calcium, the decrease of foraminifera will not result in the increase of other calcium carbonate producing organisms such as coccolithophores and pelagic mollusks (such as sea butterflies and juvenile benthic species). However, since Planktonic foraminifera are responsible for 12% of the downward particle flux, their disappearance could affect the deep sea benthos. Additionally, foraminifera produce almost 25% of the total calcium carbonate worldwide, and a decrease in that will slow down sediment formation in the long run.

As an overall conclusion, I believe that Foraminifera are more resilient to ocean acidification than many other organisms. The group will not go extinct easily, because species have evolved that inhabit the most extreme regions of the earth and have survived the loss of their calcareous exoskeleton. The production of calcite is also more effective than the production of aragonite with an increased ocean acidity under the current chemical conditions of the ocean; therefore, aragonite-producing organisms, such as corals, are likely to disappear first.

Compared to other calcite producing organisms such as many mollusks, Foraminifera are able to handle lower pH conditions because of their ability to exclude magnesium from their calcite shells. Low-Magnesium calcite is not only less likely to dissolve in water, it also allows the Foraminifera to produce calcite under more acid conditions.

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