When ecosystems undergo change it can have dramatic effects on the competition between species, food web dynamics and biodiversity. Ecosystems can undergo change by the addition of carbon dioxide into its system. This increase of carbon dioxide changes the chemistry of the seawater, known as ocean acidification. This change can have drastic effects on the pH, salinity, temperature, and aragonite that is located in the water column. These changes are currently being monitored and tested by scientists using various coupled models to try and predict the effect that global warming has on the ocean.

Since the industrial revolution there has been a significant increase in anthropogenic carbon dioxide, CO₂. This increase of anthropogenic, or human caused, carbon dioxide is from the burning of fossil fuels and deforestation. Fossil fuels are formed by a natural process of decomposed organisms. They contain high concentrations of carbon, coal, and petroleum. When fossil fuels are burned they are oxidized to carbon dioxide and water. The carbon dioxide and water are then released into air and absorbed into the atmosphere, contributing to the greenhouse gases. Greenhouse gases consist of carbon dioxide, methane, nitrous oxide and water vapor. These four components are important in the aspect of global warming, ocean acidification and ocean absorption.

The ocean absorbs approximately one fourth of the carbon dioxide that is in the atmosphere (PMEL Carbon Program). Therefore, as the burning of fossil fuels increases, the carbon dioxide in the atmosphere and ocean is also increasing. Anthropogenic carbon is stored in ocean columns. Most of the anthropogenic carbon is located at the surface. This is because it takes hundreds of years for the ocean to circulate throughout the columns. There is some anthropogenic carbon being transferred to the deep ocean by detritus. Detritus is the non-living organic material, carbon, which is falling through the water column by fecal matter and dead organisms. This absorption of carbon dioxide is causing a chemical change throughout the ocean.

This chemical change in seawater is known as ocean acidification. When the carbon dioxide is absorbed into the ocean it disassociates into ions when reacted with water. Along with the anthropogenic carbon the ocean has a natural carbon reservoir, when exchanged with the anthropogenic carbon and water the reaction forms carbonic acid (PMEL Carbon Program). Ocean acidifications change in chemistry is due to the increased concentration of hydrogen ions which initiates a chain reaction decreasing the pH, and decreasing the saturation of calcium carbonate and aragonite (*Van et. al.*, 2014). The temperature of the seawater also has an impact on the chemistry. This increase of temperature influences the dissolved inorganic carbon concentrations. Dissolved inorganic carbon is the sum of inorganic carbon which includes carbon dioxide, carbonic acid, carbonate, and bicarbonate anions. Calcium carbonate is the main component in a variety of marine invertebrates.

Corals, lobsters, clams and pteropods all rely on calcium carbonate to generate their skeleton, or shell. Immediately upon a decrease of calcium carbonate these organisms are unable to properly grow their skeleton, or shell. This leads to a lower fitness, the inability for the organisms to fully grow to be able to reproduce successfully. Coral reefs are large underwater structures that are made from stony corals. These underwater structures provide a diverse ecosystem, providing shelter and food for many marine species. However, coral reefs are sensitive to the change in water temperature, and change in seawater chemistry. Corals are also dependent on aragonite in effect to calcification rates. Calcification is the precipitation of

dissolved ions into solid calcium carbonate. A decline in calcification rates can induce a state of erosion known as coral bleaching (*Van et. al.*, 2014). An abnormal increase of sea water temperature is the main source of coral bleaching. Corals rely on a symbiotic relationship with zooxanthellae, algae, living within their tissue. Zooxanthellae carryout photosynthesis, photosynthesis provides nutrients that are used in the building of coral reefs. The warming of sea temperatures cause the corals to lose their zooxanthellae, causing the coral to lose its color and eventually die. Coral bleaching has a large effect on the environment that coral reefs provide for other species. When coral bleaching is occurring many benefits that the reef provides can be seriously impacted or lost.

Not only do coral reefs provide a diverse ecosystem for marine species, it also provides a large portion of resources for the human population. Reefs provide a natural barrier protecting coastal cities, communities and beaches. Humans rely on coral reefs for commercial fishing for food, and for millions of jobs throughout the world. Coral reefs provide potential treatments for many of the world's most prevalent and dangerous illnesses and diseases. Understanding how the change in chemistry affects the coral reefs is important in attempting to maintain its ecosystem. Using various forms of models we are able to simulate the effects of ocean chemistry by the change in anthropogenic carbon dioxide. It is important to note that pH and aragonite has a higher dependency on carbon dioxide than temperature (*Cao et. al.*, 2007).

In the modeling study [Cao et. al., 2007] ISAM-2.5D (Integrated Science Assessment Model-2.5D) is a coupled model that combines energy-moisture model, thermodynamic-dynamic sea-ice model, and marine ecosystem model. ISAM-2.5D is able to relate effects of climate change and marine biology on the uptake of carbon over a time scale to thousands of years, by simulating the uptake of heat, freshwater, carbon dioxide, and nutrients (Cao et. al., 2007). Cao et. al., [2007] ran pre-industrial atmospheric carbon dioxide concentrations, for the years before 1765. Between the years 1765 and 1990 the model was initiated with observed carbon dioxide concentrations, and from 1990 to 2500 the model was initiated with prescribed carbon dioxide emissions. The carbon dioxide emissions include both net carbon dioxide from the terrestrial biosphere and fossil fuel carbon dioxide. In the simulation where ocean chemistry is only influenced by increased atmospheric carbon dioxide, it followed the predicted carbon dioxide concentration pathways. Simulation where the ocean chemistry is affected by changes in the atmospheric carbon dioxide and climate are predicted to have higher carbon dioxide concentrations than the simulation that is only influenced by atmospheric carbon dioxide. This results in a reduction of oceanic carbon dioxide uptake that is associated with increased temperature. The direct temperature effect dominates the indirect dissolved inorganic carbon seen in Figure 1. The model predicts an increase of sea surface temperature and a decrease in the sea surface salinity, seen in Figure 1. As the concentration increased the ocean surface pH and aragonite is predicted to decrease. When the climate change is included in the prediction models it amplifies the projected simulations. Cao et. al., [2007] reports that a predicted 0.47 unit reduction in surface pH and a reduction of saturation, with respect to aragonite, to 1.39 from the pre-industrial values. These results of ocean acidification will have an impact on the marine ecosystems, coral reefs, through the lowering of pH and the carbonate saturation state.

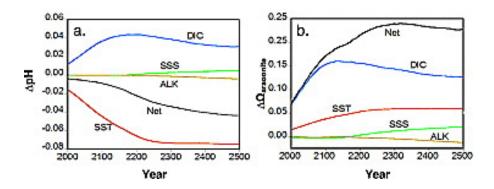


Figure 1: Changes in (a) pH as a result of changes in dissolved inorganic carbon (DIC), sea surface salinity (SSS), alkalinity (ALK), the combined effect of changes in SST, SSS, ALK, and DIC (NET), and sea surface temperature (SST). Changes in (b) aragonite as a result of changes in the combined effect of changes in SST, SSS, ALK, and DIC (NET), dissolved inorganic carbon (DIC), sea surface temperature (SST), sea surface salinity (SSS), and alkalinity (ALK). Changes in (a) and (b) are plotted for the simulation with changes in the atmospheric carbon dioxide and climate change [Cao et. al., 2007].

Climate models are also used in predicting when severe coral bleaching events will occur in the future. In the modeling study [Van e. al., 2014] data was collected from coupled models in the Coupled Model Intercomparison Project 5 (CMIP5). These model outputs were reduced to contain only coral reef locations. These locations were obtained by the UNEP-WCMC's Millennium Coral Reef Mapping Project Seascape. Within these locations the reefs were grouped into six latitudinal ranges. The climate models showed that there is approximately a thirty year range in the projected year in which severe coral bleaching will occur at 95% of all reef locations. A total of 90% of all reef locations are expected to experience bleaching prior to the year 2055. The reef locations located near the equator are to experience coral bleaching before the reefs located at higher latitudes. The average year in which severe coral bleaching starts to occur annually with respect for the six zonal areas are 5,6,9,12,14 and 19 years (Figure 2). Van et. al., [2014] reports that the decline in aragonite projected between 2006 and the onset of annual severe bleaching ranges from -.01 to -1. Declines in calcification range from 1% to 21% between 2006 and the onset of annual severe bleaching. The onset of annual severe bleaching sets a time frame between current day and the year that coral reefs are severely bleached on an annual basis to the point of extreme ecosystem loss. This climate model illustrates the impact of aragonite on the coral reef ecosystems and the rapid onset of coral bleaching to the ecosystem. In the Caribbean 37% of reefs are already found to be net eroding (Van et. al., 2014). This net eroding will have a large impact on human resources from the depletion of coral reefs, and on the marine species and algal communities.

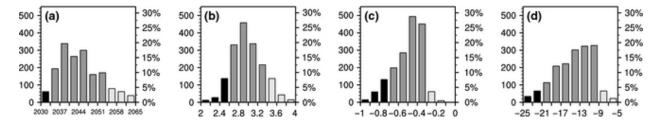


Figure 2: Histograms of the number and percentage of coral reefs for the year when annual severe bleaching occurs, 2030 to 2065 (a). The absolute value of aragonite when annual severe bleaching occurs (b). The projected absolute value of aragonite (c) and the percentage (d) change in aragonite between 2006 and the onset of annual severe bleaching.

Changes in carbon chemistry in the seawater can affect the carbon fixation by photoautotrophs. Photoautotrophs are organisms that obtain energy from sunlight to convert inorganic material, carbon, into organic material, such as biosynthesis and respiration. Benthic, or bottom dwelling, photoautotrophs due to ocean acidification can induce a change in competition and dominance that can affect the ecosystems. Some cyanobacteria grow well in carbon dioxide rich environments. Macroalgal communities are located in ecosystems along coastal communities. They also provide food, shelter and are sensitive to anthropogenic disturbances.

Porzio et. al., [2011] assessed Macroalgal communities in response to marine ecosystems to ocean acidification. The sampling was conducted off the coast of Castello Avagonese in the Gulf of Napa, Italy. Out of the 101 macroalgal taxa there were three species groups, i.e. 'crustose', 'turf', and 'erect'. Sections were determined by species number, percent cover of species, species diversity, and percentage cover of the three species groups 'crustose', 'turf', and 'erect'. The data showed that a highly significant species diversity reduction at carbon dioxide concentrations increased. A clear shift in species was evident along the carbon dioxide gradient. There was also evidence of a difference in species richness and abundance that affected the community structure. *Porzio et.al.*, [2011] reports that the 'crustose' algae was abundant at mean pH of 7.8, but was reduced in the areas of the highest carbon dioxide concentration levels. There was a 25% biodiversity loss within these macroalgal species. However, some of the algae species had no negative effects on reproduction at the high carbon dioxide concentration levels, Rhodophyta and Chlorophyta. Several calcitic and aragonitic species of algae were able to settle and grow at high carbon dioxide concentration levels that are expected as the global ocean acidification due to anthropogenic carbon dioxide. Carbon dioxide enrichment caused shifts in the abundance of whole morphological groups, indicating that a rise in carbon dioxide levels will alter ecosystems, including food web dynamics and the cycling of carbon and nutrients along with biodiversity (*Porzio* 2011).

The increase of anthropogenic carbon dioxide into the atmosphere from the burning of fossil fuels also causes an increase of carbon dioxide in the ocean. As previously stated this increase of carbon dioxide changes the chemistry of the seawater, known as ocean acidification. This change can have drastic effects on the pH, salinity, temperature, and aragonite that is located in the water column. These changes are currently being monitored and tested by scientists using various coupled models to try and predict the effect that global warming has on the ocean. These effects on the chemistry can control the bleaching of coral reefs and their ecosystem. The change in the ecosystem can have drastic effects on the competition between species, food web dynamics and biodiversity.

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