Uptake of Anthropogenic CO_2 and its Effect on Recent Changes of Calcite and Aragonite Saturation in the Northern Pacific from 2006-2015

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Abstract

As one of the largest carbon sinks in the world, the ocean takes up a large portion of carbon dioxide in the atmosphere. As described through seawater-atmospheric equations, the pH of the ocean has significantly decreased as a result of this interaction. This decrease in pH has negatively affected the availability materials like aragonite and calcite, which are vital for organisms that utilize them. The northern Pacific has been shown to have extra susceptibility to this change in pH due to the increased uptake of carbon dioxide. Data sets from 2006 and 2015 were compared in this location in order to determine the change in aragonite and calcite in a context of increasing carbon dioxide levels. The 'omega' value was used as a unit to determine the saturation value of both aragonite and calcite. This study ultimately shows that not only has the difference between omega values from 2006 to 2015 remained the same, but has in fact increased in deviation in recent years when compared to data from the 1990's. This shows that the shoaling of these saturations is larger than previously anticipated, and may be a significant issue in the future if organisms in this region start to die off and affect the food web.

Summary

Since the dawn of the industrial revolution, human activity has significantly increased the amount of carbon dioxide put into the atmosphere. This addition has had and will continue to have dire consequences on various components on the global environmental system. Due to the interaction of exchange of carbon between the boundary of the ocean and atmosphere, the ocean is one of the largest systems affected by this change. As a result of this increase, a problem called ocean acidification is created in which the pH of the ocean is driven down through a series of reactions that include seawater and carbon dioxide. Through this reaction, other important materials utilized by organisms in the ocean are affected in negative ways. Previous studies have found that the depth at which both aragonite and calcite are saturated has become shallower over time, hence less available for the organisms that need them. This study aims to see if that shoaling, or shallowing, of the depths at which aragonite and calcite saturation has steadily become less shallow over time, or if this problem has increased in recent years with the larger increase of atmospheric carbon dioxide.

Introduction

In recent history, carbon dioxide emissions have risen dramatically. CO_2 concentrations have risen from 280 ppm (parts per million) in early greenhouse gas emissions, to greater than 400 ppm in 2020 (shown in Figure 1). It is estimated that the exponential growth rate of carbon dioxide in the atmosphere has more than doubled in the past 40 years [*Hofmann et al*. 2008]. Approximately 1/4 of this carbon dioxide in the atmosphere has been absorbed at the ocean-atmosphere boundary, which in turn distributes carbon dioxide within the oceans. This interaction can be described by Henry's law (*eq 1*), which shows the concentration of the dissolved gas equal to the coefficient multiplied by the partial pressure of the gas in the atmosphere. In the equation, carbon dioxide is shown to be taken up by the ocean based on its solubility and overlying partial pressure, which in turn allows for it to react with seawater (*eq 2*). The ocean takes up to 90 percent of the excess energy from the atmosphere, while also up taking one fourth of excess carbon dioxide, and, due to the relationship in the ocean-atmosphere equation, means the increase in carbon dioxide into the atmosphere results in a high amount of carbon dioxide into the ocean [*Calderia and Wickett,* 2003]. Carbon dioxide in the ocean is responsible for a phenomenon known as ocean acidification, which decreases the overall pH of water through the system of equations shown below, and restricts the calcification process that many marine organisms utilize by a higher concentration of bicarbonate over carbonate. [*Erez et al.* 2010]. This CO_2 and seawater relationship in shown to create a weak acid in the form of carbonic acid. (*eq 2*). Other studies have also examined the overall increasing acidity of the ocean. The increase of dissolved carbon dioxide and carbonic acid, simply put, decreases the pH of the water it inhabits through the equilibrium equation given in equation 2. Over the next century, it is estimated that the change to surface pH is projected to decrease by 0.3-0.5 units, the largest change in the last 20-200 million years [*Feely et al. 2004*]. Through both [*Feely et al. 2004*] and [*Burton and Walter, 1987*], one can see the impact of ocean acidification on the world's ocean, and its effect on local organisms and the acidity of the ocean.

Equation 1 (Henry's law)

$$[A(aq)] = K_{H,C} \, x \, P_A$$

Equation 2 (CO_2/Seawater relationships)

$$CO_2 + H_2O \leftrightarrow H_2CO_3 \leftrightarrow H_+ + HCO_{3-} \leftrightarrow H_+ + CO_{2-}$$

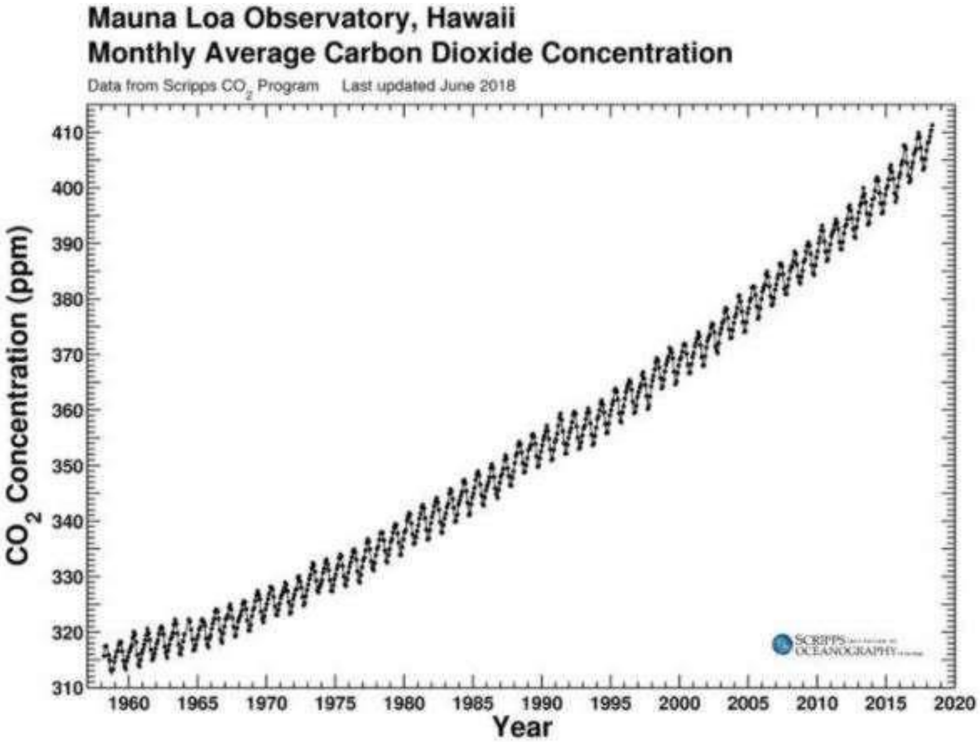


Fig 1: The “Keeling curve” (Atmospheric concentration of CO_2 in parts per million (PPM) measured at Mauna Loa) [Scripps CO $_2$ program, 2020]

[*Feely et al. 2012*] measured the changes of both aragonite and calcite in the north Pacific, and reported a shoaling of aragonite and calcite values across depth values from 1992 to 2006. The findings made by this study were conclusive that this rate had become quicker over time, and through this study, we aimed to see if that rate has further increased or if the rate had stayed the same in roughly the past decade. In the northern Pacific area, there are many planktonic organisms that utilize either calcite and aragonite, materials that are affected by ocean acidification. Pteropods, for example, are one of these organism’s that use aragonite for survival in the environment. Saturation, a measurement of complete dissolution into a liquid, can often describe the abundance of these materials in seawater. Low saturated aragonite values correlate to a lower percentage of pteropods survival [Burton and Walter, 1987]. Since pteropods are low on the food chain, most of the food web in the north Pacific will be negatively affected if pteropods are negatively affected.

The value ‘omega’ developed in [*Lewis and Wallace, 1998*] will be used to analyze the saturation states of both aragonite and calcite. The equation is described by the concentrations of both calcium and carbonate, over the respective stoichiometric solubility products of both aragonite and calcite in their own separate calculations. This omega value will show the dependence on calcium and carbonate, both of which are heavily influenced by the severity of ocean acidification, which impacts the availability of both. As the concentration of calcium and carbonate decreases, the resulting value for omega will also decrease, meaning the saturation of calcite and aragonite will most likely be low in areas that are affected by ocean acidification. The solubility product of both materials is also utilized in the omega equation. This value can be affected by seawater properties in different areas in the ocean (i.e. temperature), so extra metadata must be taken in order to fully comprehend omega values in zones of the northern Pacific.

$$\Omega arag = \frac{[Ca2+][CO2-]}{Ksp\ arag}$$

$$\Omega cal = \frac{[Ca_{2+}][CO_{2-}]}{Ksp\ cal}$$

Though the occurrence of ocean acidification is well observed and understood in the field of oceanography, it is relatively unknown how the effect of the increase on carbon dioxide in the world’s ocean affects the rate at which this shoaling phenomenon of aragonite and calcite carries out. This study aimed to answer the following: How does the increase of anthropogenic carbon dioxide effect the saturation states of calcite and aragonite at constant depths in the water column, and in a context over time, do those values change? Based on past information and studies, it is likely that the overall saturation states of both calcite and aragonite should decrease with the increase of atmospheric CO_2. I also hypothesized that the saturation depths will remain shallow over time, but the overall amount of saturation of both calcite and aragonite should be seen to decrease in recent years. The null hypothesis to this question would show no change over time to the saturation values of both aragonite and calcite, and that the increase of anthropogenic carbon dioxide has no effect on either the saturation amount or depth profiles of calcite and aragonite.

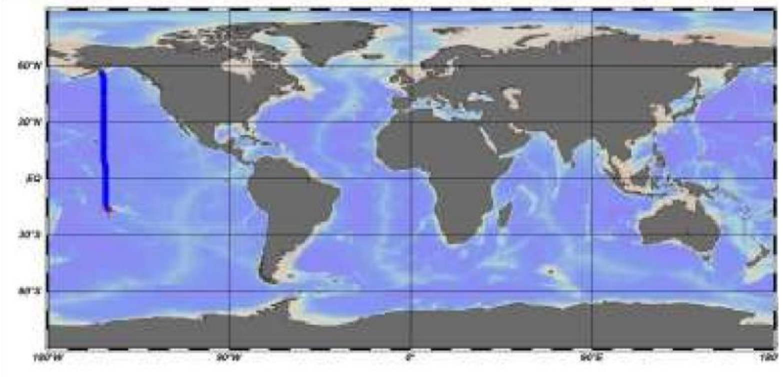
Methods

The CCHDO (cchdo.ucsd.edu accessed on 1/5/21) database was used in order to access the P16N cruises through the northern Pacific from 2006 and 2015. The P16N cruise in 2015 was taken over a one-month period from May to June, while the 2006 cruise occurred from February to March. Both cruises followed along a longitude transect of 152°W, and stopped for data measurements roughly every 0.5° of latitude. Bottle data from a CTD method was the primary form of data used in this analysis, and had been uploaded to the CCHDO database approximately six months after cruise termination, while data access for this study started in December of 2020. Figure 2 A and B shows the region in which the P16N data was acquired through the longitude transect, while Fig. 3 and 4 show the depth profile of calcite and aragonite in the same area, captured from [Feely et al. 2012]. Other studies like [Pilcher et al. 2019], and [Sabine et al. 2002] have reported other well-formed resolutions of calcite and aragonite saturation as well, with similar graphs to the ones shown in Fig. 3 and 4.

In calculating omega saturation values in conjunction with carbonate and calcium values, a program was designed and utilized by a paper by *Lewis and Wallace* [1998], which has further been used by other paper that have analyzed the relationship of saturation states of calcite and aragonite. Fig. 3 and 4 are depictions of these relations in utilizing the CO2SYS program in the Feely paper [*Feely et al.* 2012]. Omega values were plotted against the depths at which they were taken to give a depth profile of the saturation values of both materials, while also having other panels examining the changes in these values over time. The CO2SYS program uses python and MATLAB code to synthesize calcium and carbonate values though the system of equilibrium equations, taking measurements of carbon dioxide, pH, and total alkalinity, and converting them into values of omega [*Lewis and Wallace,* 1998]. There are several different values that can be used in this program, but this study used alkalinity and total carbon values taken from bottle data on the P16N cruises. Along with the Millero constant, these values have been input into the CO2SYS program in order to find omega values in regions of interest.

In order to create plots like Fig. 3 and 4, Ocean Data View was used to synthesize both the P16N cruise data from both years and the CO2SYS program. Ocean Data View supports the use of the program in its “derived variables” section, and after inputting values of alkalinity, total carbon, pressure, temperature, and salinity, outputs values of omega that can be analyzed at any point along the cruise track. Graphs were made at an extent from this software, and excel was utilized after an export of calculated omega values were made in the software.

2A



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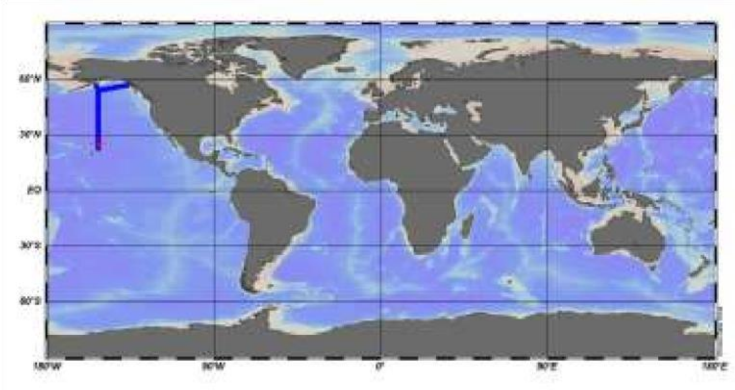
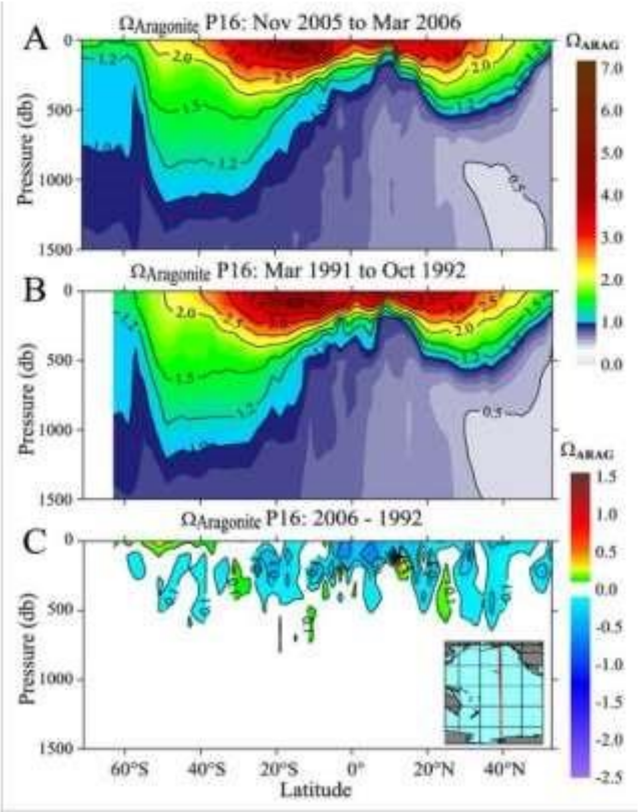
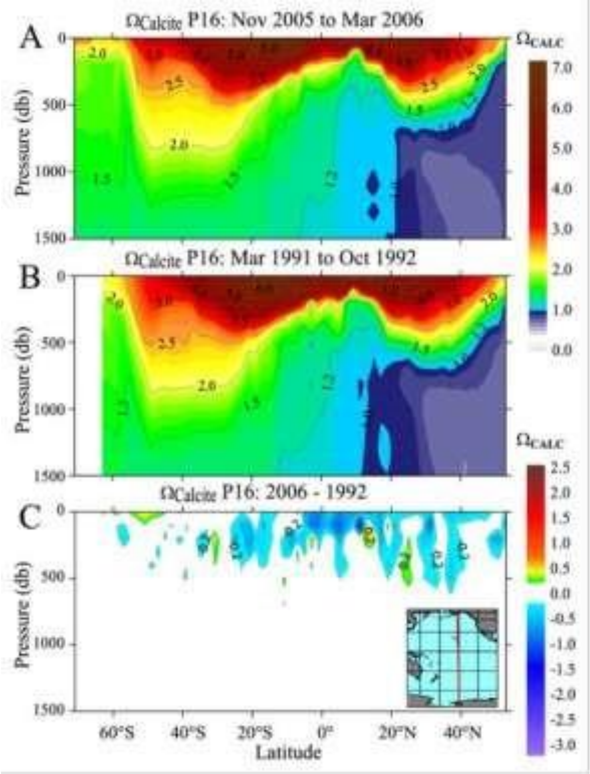


Figure 2 A and B: Cruise tracks from P16N 2006 (A) and P16N 2015 (B) along 152°W. Bottle data from CTD measurements uploaded the CCHDO from both cruises.



va



Figures 3 and 4 show depth profiles of aragonite and calcite (omega) saturation in northern Pacific over a latitude section from 60 degrees south to 40 ***degrees*** *north*

Panel 3A: Aragonite omega values as related to pressure (depth) 2005-2006
Panel 3B: Aragonite omega values as related to pressure (depth) 1991-1992

Panel 3C: Differences between figures 3A and 3B
[*Feely et al.* 2012]

Panel 4A: Calcite omega values as related to pressure (depth) 2005-2006
Panel 4B: Calcite omega values as related to pressure (depth) 1991-1992

Panel 4C: Differences between figures 4A and 4B
[*Feely et al.* 2012]

Results

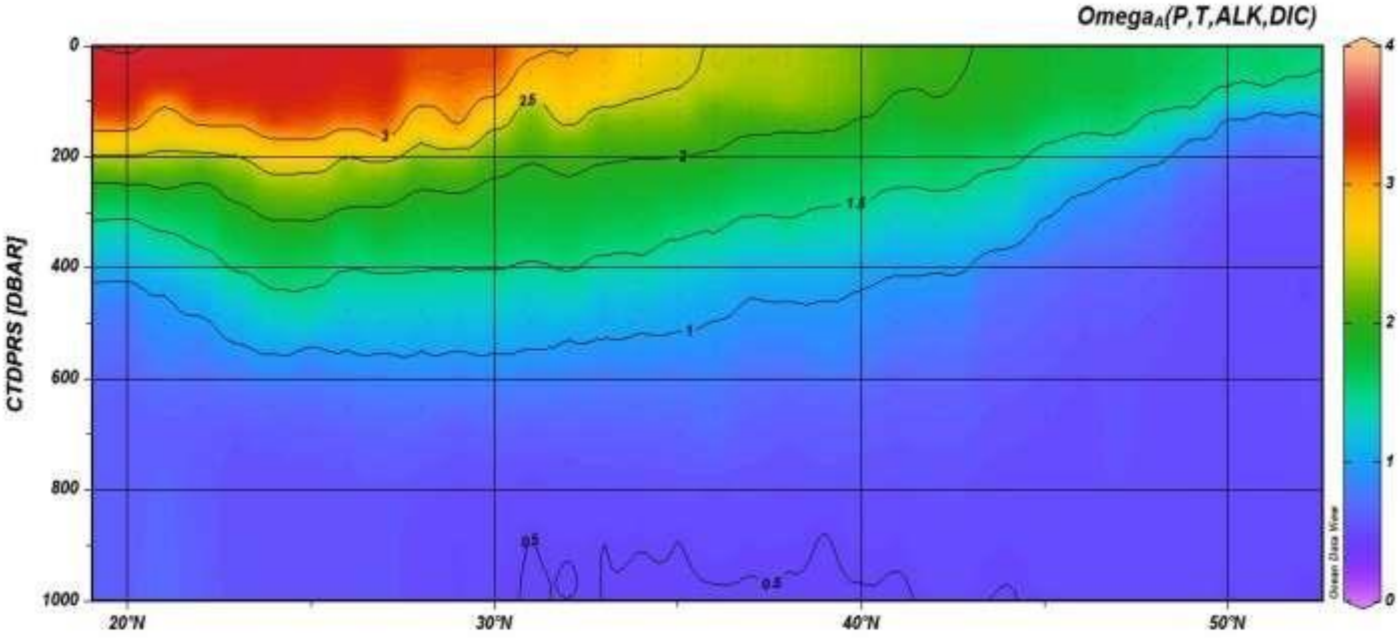
Overall, these figures show that the shoaling of aragonite and calcite is occurring at a quick rate, which varies at differing location in the pacific. The values of omega at the surface of the ocean (above a depth of 1000 meters) are shown to have been becoming smaller over a constant depth range. The data from 2006 was shown to have higher omega values at similar depth ranges than the data in 2015. In addition, the differences between the two datasets are larger in proximity to the subtropical gyre. Stations at 25° N were shown to have a considerably larger difference in omega values than stations at 35° N and 45° N.

The first set of graphs produced were comparative contour graphs similar to the ones shown in Fig. 3 and 4 [*Feely et al. 2012*]. Fig. 5 panels A-D map the saturation depths of both calcite and aragonite over a latitude section from 20° to 50° north. Through use of contour line comparison, we can see that between the two values in different years, the omega value of both aragonite and calcite has become shallower over the ten-year time difference. Depths at 200 meters measured an aragonite omega value of around 3 on the y intersection of the graph in 2006 and a value of around 2.5 in 2015. Depths under 600 meters remain relatively unchanged in all panels, and as a result, all figures were cut down to magnify the variation in the upper 1000-meter ocean over time.

Fig. 6 panels A-F show specific and more measurable differences between the two cruises at three different stations in specific locations across the latitude section. Although there is a difference between years in all stations, the biggest difference in omega values remain in the 25-degree north station as compared to the 35- and 45-degree stations. A line was also plotted to show the value that organisms in the northern Pacific typically need to utilize to survive (approx. omega =1). Fig. 7 A-C reinforces this finding by taking the aragonite difference between the 2015 and 2006 data. The larger negative omega values in this figure indicate that the 2015 data was a magnitude smaller than the 2006. The 25degree north was shown to have the largest difference by an omega magnitude of about 0.5.

In a closer look of Figures 5 through 7, it is obvious that there are two main points of interest in differences between the 2006 and 2015 P16N cruise tracks; shallow water and proximity to the equator. First, Fig. 5 visually shows the shoaling of both aragonite and calcite omega values over a depth profile across the latitude section. The omega values show to be more affected towards the surface ocean, and show almost no noticeable difference under that ocean surface layer. Changes closer to the surface in Fig. 5 show that the omega values change more from 2006 to 2015 at depths above 600 meters as compared to under 600 meters. For example, an omega value of 3 occurs at a roughly 150-meter depth in 2006 and roughly a 125-meter depth in 2015. We can subsequently say that the same omega value has 25-meter difference over nine years, a shoaling rate of 2.79 meters per year.

5A: *2006*



5B: *2015*

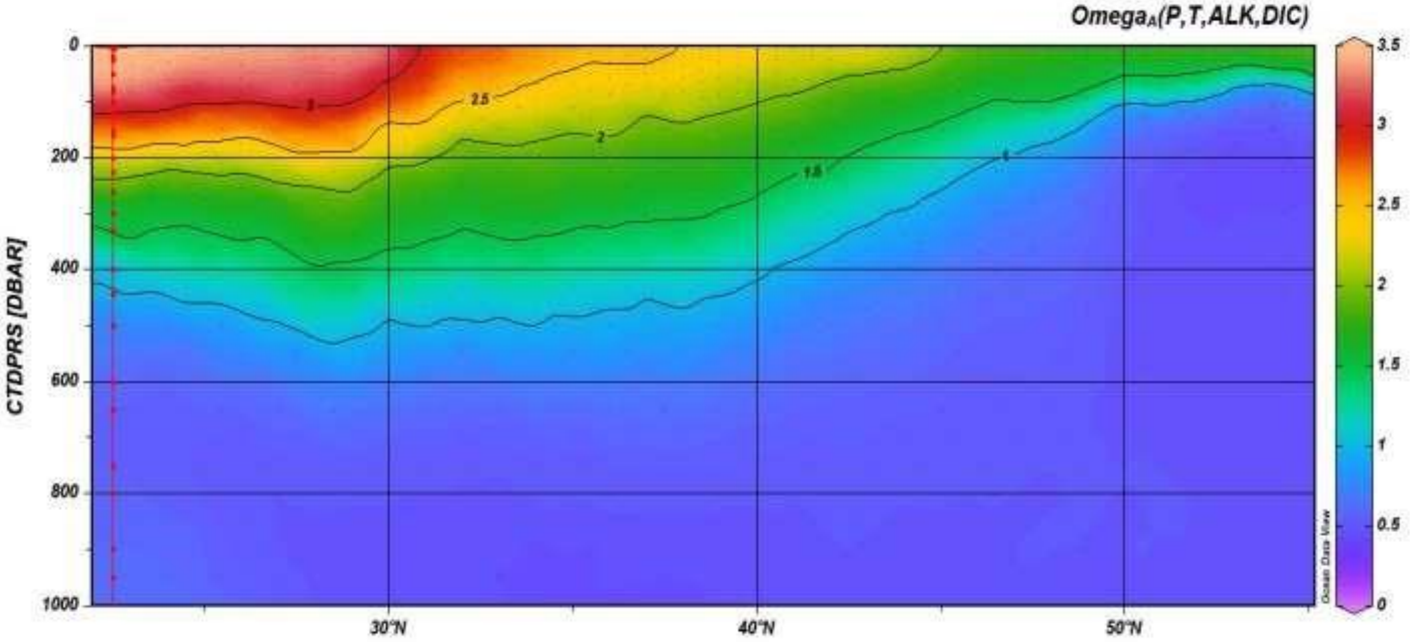
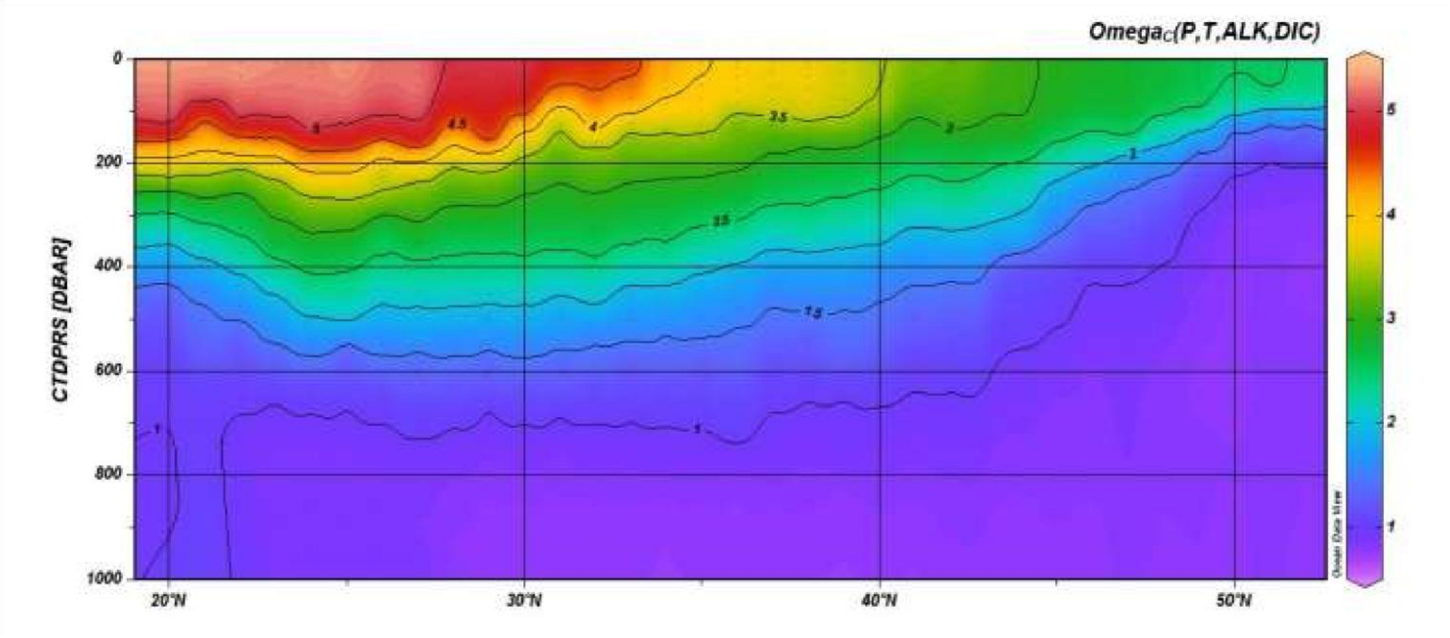


Figure 5: Aragonite saturation values measured in omega over a depth of 1000 meters on the y and latitude section from 20-50° N on the x. Values extrapolated to show a color gradient with contour lines

5C: 2006



5D: 2015

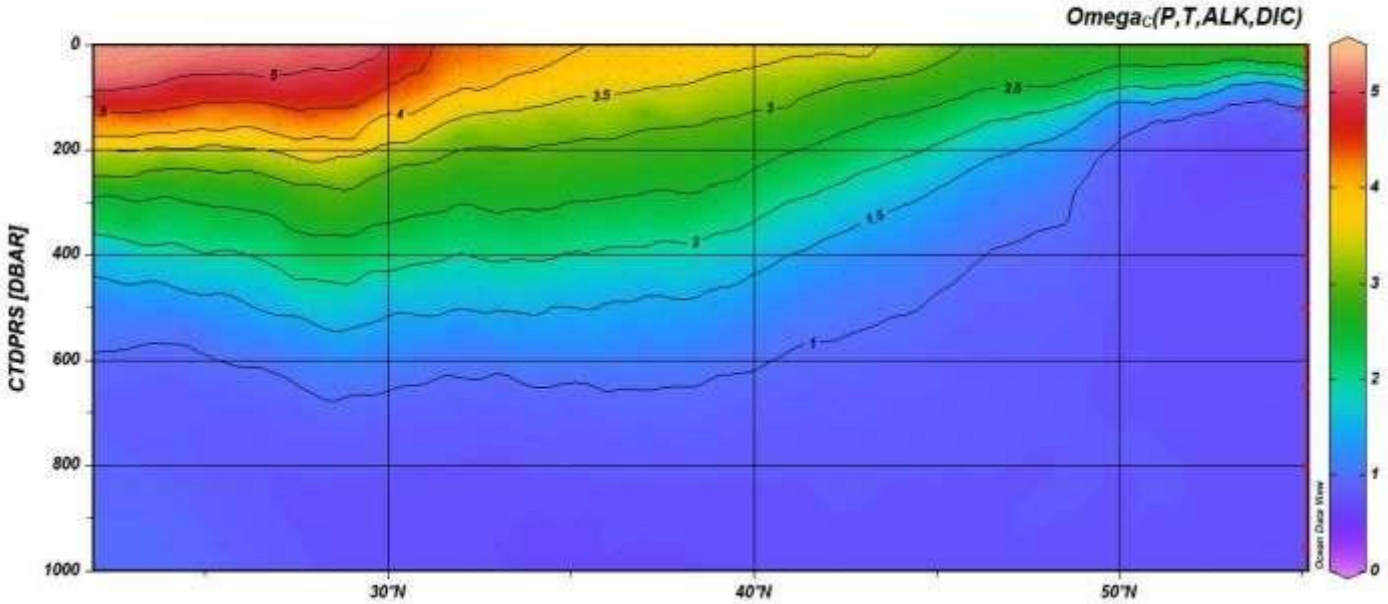


Figure 5: Calcite saturation values measured in omega over a depth of 1000 meters on the y and latitude section from 20-50° N on the x. Values extrapolated to show a color gradient with contour lines

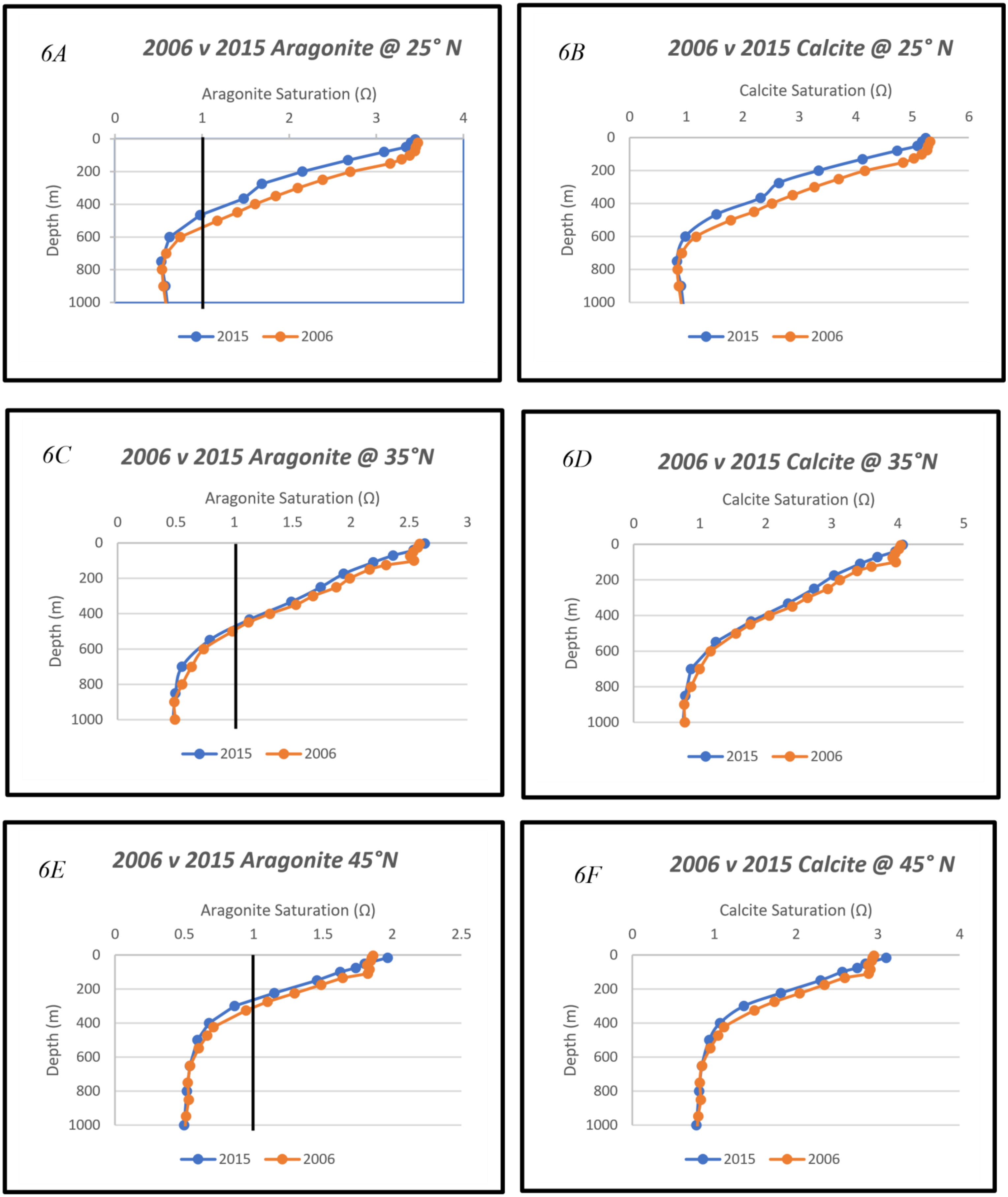


Figure 6: Figure panels A-F show the 2015 and 2006 data as a function of depth on the y and omega saturation on the x..Vertical line at approx. omega =1 shows required value for organisms to utilize omega aragonite values

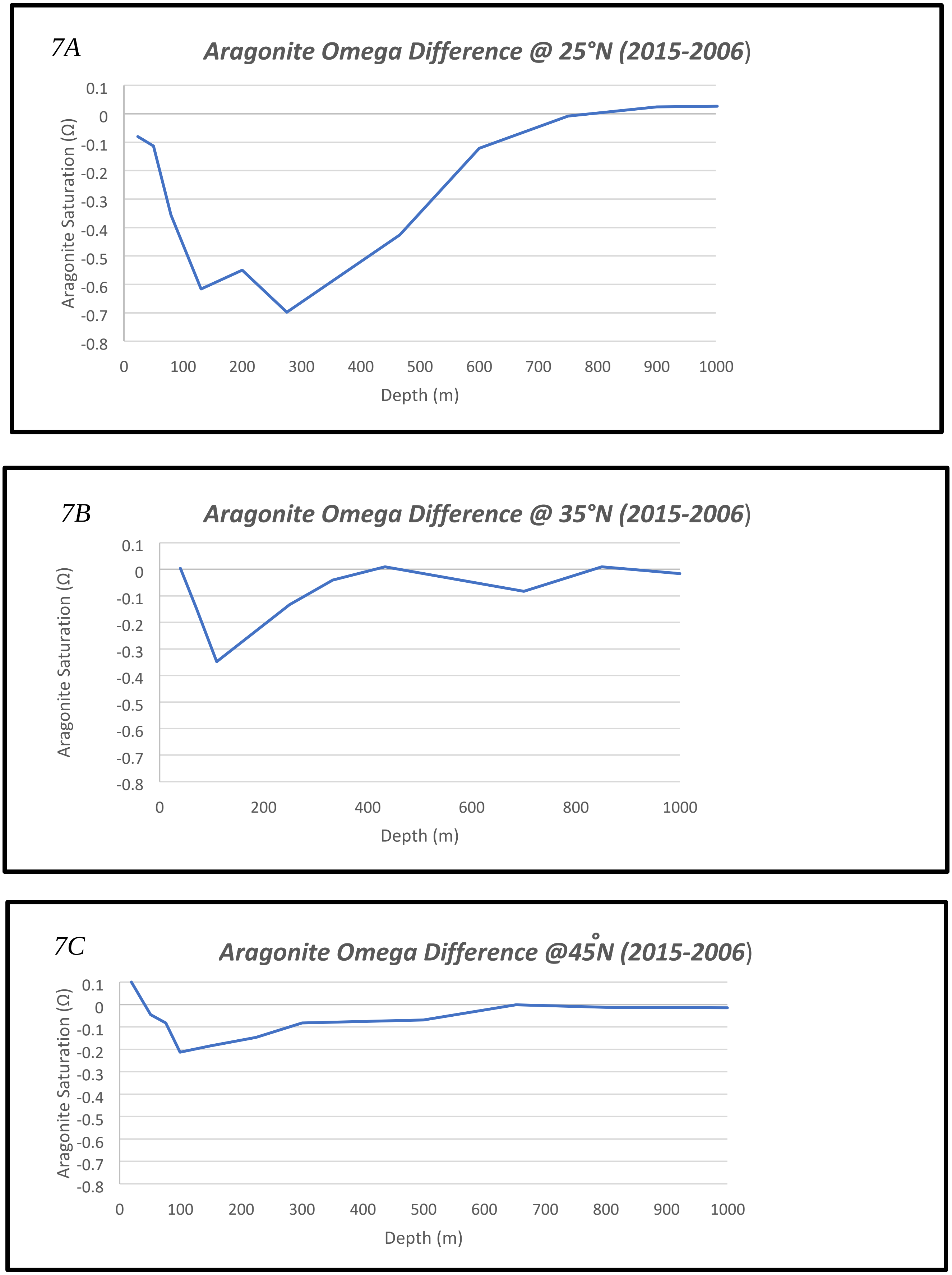


Figure 7: Figure panels A-C show the difference between aragonite saturation in omega from 2015 and 2006. The 2006 data was subtracted from the 2015 data

Discussion

Both of the reasons why the values of omega are different over time are supported and predicted by past studies on the same subject. Fig. 3C and 4C taken from [*Feely et al. 2012*] only show significant differences above 500 meters, with the biggest changes occurring in the subtropical gyres around 25° N. Feely also only observes decreases in the saturation state, and almost never shows an increase in any area shown over the tested section. This finding is also shown in Fig. 7, showing values that continue to decrease in the upper 1000 meters from 2006 to 2015. Although the [*Feely et al. 2012*] study synthesized data from 1992 to 2006, the results from this study ten years later follow the same trends as ones in the past. Although these trends are similar, the amount of variation from [*Feely et al. 2012*] are not exactly the same as the variation measured in this study. In Fig. 3C, an approximate change in aragonite saturation measured at an average omega difference of -0.1 in the 25° N region, while our findings show an average of a -0.265 omega difference in that same region (both averaged over a depth range of 1000 meters). Regardless of reason, these results show that the difference between approximately equal time periods are becoming increasing different as time progresses. The other locations plotted against the differences were not as large as the 25° zone, but still showed a small difference between the two time periods.

In order to establish credibility to these findings, graphs were also created with potential density on the y-axis instead of depth to check that isopycnal movement was not responsible for this change. No significant findings were made, creating a better faith in the conclusions drawn from this study. Although the conclusions of these findings are also apparent, going out into the field to take personal measurements of these values would allow for a more direct and accurate reading of omega values in the northern Pacific. The data taken from P16N are adequate in this study, but measurements taken purposefully for this analysis alone would allow for more flexibility and obtain data where the current data is lacking. A timescale shorter than the one shown in this study could show other details from an enhanced resolution. Data was extrapolated in areas where it was absent in the database, and consistent and specific measurement in this area would fix this issue.

Conclusion

Because aragonite and calcite are vital to the organisms that utilize them, the conclusion that the shoaling rate of these materials are increasing is massively important to the health of food webs in these areas. Values of omega =1 were shown to occur at a shallower depth at 2015 than they previously did in 2006. Understanding of this shoaling could allow for a redirection of focus and effort into solving this problem as it most likely becomes larger in the future. Taking all of this into account, still, these findings from this data are adequate enough to show the difference between current conclusions and conclusions drawn from past studies.

Consistent with the hypothesis, the saturation depth of both aragonite and calcite were shown to become shallower at constant omega measurements across a latitude section, and furthermore, were shown to be shoaling at a faster rate than in the recent past. Although seeing the decrease in depth of aragonite and calcite were expected, what is surprising is that the shoaling has become noticeably larger in recent time. When doing preliminary research, it was expected that this data would show similar to previous studies (i.e., [*Feely et al. 2012*]), but it was not expected that the rate has doubled in the past 9-10 years. As a follow up to further prove these findings accurate, researchers should wait until 2024 to obtain data to have similar time periods of both this study and the Feely study. Findings in future studies should show that the shoaling rate is still progressively increasing, and the average value at 25°N should be greater than the average found in this study. In addition, further studies in other areas of the global ocean could be helpful in further understanding this problem, and a backing of these findings in other areas would also help show how this problem is spread across the globe.

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