

**INVESTIGATION OF CHANGING SEAWATER CARBONATE  
CHEMISTRY NEAR DEEP-SEA CORAL BEDS**

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## **ABSTRACT**

Investigation of Changing Seawater Chemistry by Deep-Sea Coral Beds due to Climate Change

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Anthropogenic impacts on the global ocean, including increasing carbon dioxide levels and sea surface temperatures, have significantly changed the chemistry of the seawater itself, by acidifying waters, creating low oxygen zones and changing nutrient levels. Deep-sea corals are vulnerable to these environmental changes, as calcification of their skeletons becomes more difficult under acidified conditions. Nutrient availability from the surface may also change and affect the food supply to deep-sea corals. This study analyzed the current chemistry of seawater around deep-sea coral beds in the Northwestern Hawaiian Islands with data from two cruises conducted in 2014 and 2015 and compared it to historical measurements from the 1990s from the same region taken from the World Ocean Circulation Experiment (WOCE). The possibility of shoaling calcium carbonate ( $\text{CaCO}_3$ ) saturation horizons due to climate change was assessed. The saturation horizons of two forms of  $\text{CaCO}_3$ —calcite and aragonite—were found to have shoaled since the 1990s. Aragonite saturation horizons shoaled from 747 to 652 m and calcite saturation horizons shoaled from 1006 to 854 m. The shoaling of aragonite saturation horizons over time was consistent for two different methods for calculating horizon depth while shoaling of calcite saturation horizons was only shown for one of the two methods. Shoaling rates from the 1990s to

the 2010s has also accelerated, compared to rates from the preindustrial era to the 1990s. The aragonite saturation horizon is shoaling 28 times faster and the calcite saturation horizon 32 times faster than shoaling rates determined in the 1990s. This study found saturation horizons of calcite and aragonite are becoming shallower faster, which means that deep-sea corals that were previously in saturated waters are now experiencing undersaturation.

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# CHAPTER I

## INTRODUCTION

### Deep-Sea Coral Characteristics and Communities

Deep-sea corals, or cold water corals, create the most three-dimensionally complex habitats in the deep ocean (Roberts, 2006) and support diverse communities of fish, invertebrates, and microbial communities (Baco, 2007; Husebø et al., 2002; Yakimov, 2006; Alongi, 1992). These organisms can create large reefs (scleractinians) or live dispersed in a bed (octocorals) (Baco, 2007). Some species of deep-sea corals, known as precious corals, are commercially harvested and their skeletons are made into jewelry (Baco, 2007). Deep-sea corals are found between 200 and more than 6500 m depth worldwide (Baco, 2007). These invertebrates do not depend on sunlight, as they are azooxanthellate and do not require the symbiotic relationship with zooxanthellae, algae living in coralline tissue, which shallow warm water corals benefit from (Roberts, 2006). Instead, deep-sea corals rely on filtering plankton and detritus as their main food source (Roberts, 2006; Biber et al., 2014). However, deep-sea corals are not limited to areas with highly productive surface waters because food may be transported via currents from elsewhere (Guinotte and Davies, 2014). Although reproduction is still not understood among most deep-sea corals, a study in the North Atlantic found that the reproduction of the deep-sea coral *Lophelia pertusa* is triggered by an influx of organic material from the surface (Waller et al., 2005). Deep-sea corals are slow-growing but can live for thousands of years, with one *Leiopathes* sp. specimen aged at  $4265 \pm 44$  cal. yrs. (Roark et al., 2009). As a result, the skeletons of deep-sea corals can be used in paleo-oceanographic research of past climates and oceanic conditions (Roark et al., 2009).

Deep sea corals can form proteinaceous skeletons or calcareous skeletons in the form of high magnesium calcite, aragonite, or calcite (Roark, 2009; Baco, 2007). Many deep-sea coral beds and reefs are found on seamounts, as the shallower depths shelter the calcareous organisms from inhospitable seawater chemistry conditions that would inhibit the maintenance and growth of their skeletons in deeper waters (Roberts, 2006; Tittensor et al., 2010). These underwater mountains can create unique localized conditions by wrapping currents around their outcroppings (Roberts, 2006). This can trap gametes and larvae, limiting species dispersal and enhancing endemism between different clusters of seamounts in the same area (Roberts, 2006; de Forges et al., 2000). In the Hawaiian Archipelago, populations of the deep-sea precious coral *Corallium lauense* on eight different seamounts were found to be genetically diverse but possibly be suffering from inbreeding depression as a result of the limiting dispersal (Baco et al., 2006).

### **Anthropogenic Influence on Deep-sea Corals**

The anthropogenic production of excess carbon dioxide (CO<sub>2</sub>) into the atmosphere is impacting the ocean in several ways including ocean acidification (OA), warming, and deoxygenation (Feely et al., 2004; Hönisch, 2012; Keeling et al., 2010). Climate change can therefore exacerbate the natural conditions of the environment that deep-sea corals live in: deep hypoxic waters with high CO<sub>2</sub> concentrations and low pH. Deep-sea corals also have extremely low growth rates, resulting in low resilience and recovery rates (Roberts et al., 2006). One study found that a black coral had only grown 8 to 22  $\mu\text{mol}$  per year in a span of 2,000 years (Prouty et al., 2011). In the northeast Atlantic, fish populations benefitted from a marine protected area but there was very little recovery or regrowth in deep-sea corals over eight years (Huvenne et al.,

2016). Deep-sea coral communities are therefore highly susceptible to damage from anthropogenic activities including fishing, drilling, and global climate change.

### *Fisheries and Drilling*

Seamounts are particularly susceptible to exploitation as the underwater mountains attract aggregates of fish and support deep-sea coral beds (Morato et al., 2006; Baco, 2007). Historically, the fish populations and precious corals were harvested using trawls that would scrape the bottom regardless of what species was being fished, leaving nothing behind except the seafloor (Grigg, 1993; Roberts, 2006; Baco, 2007). Bottom trawling is therefore one of most damaging fishing techniques to benthic communities (Morgan and Chuenpagdee, 2003). In the 1980s, the precious corals in the families *Corallium* and *Antipathes* were listed by the Convention on International Trade in Endangered Species of Wild Fauna and Flora (CITES) as potentially threatened if regulations on harvesting and trade were not introduced (Appendix II). As of this publication, no species of deep-sea corals are listed as threatened or endangered. Drilling for oil and gas can also impact benthic communities. Deep-sea corals can be physically damaged by exploratory drilling or drilling equipment (Roberts et al, 2006; Lumsden et al., 2007). Discharges of sediment or leaking of drilling fluids can also smother corals (Lumsden et al., 2007).

### *Ocean Acidification*

OA occurs when increasing dissolved CO<sub>2</sub> reacts with seawater to form carbonic acid (H<sub>2</sub>CO<sub>3</sub>), lowering pH and carbonate ion (CO<sub>3</sub><sup>2-</sup>) concentrations. OA is currently threatening calcifying organisms with skeletons made out of calcium carbonate (CaCO<sub>3</sub>), including deep-sea corals, because production of biogenic CaCO<sub>3</sub> is slowed and dissolution is enhanced as CO<sub>2</sub> increases and CO<sub>3</sub><sup>2-</sup> and pH decrease (Feely et al., 2004; Baco, 2007). Aragonite and calcite are two mineral forms of that make up deep-sea coralline skeletons (Baco, 2007; Roark, 2009). The

saturation state ( $\Omega$ ) of these minerals signifies the thermodynamic potential to precipitate or dissolve in water. When  $\Omega > 1$ , seawater is supersaturated and precipitation of aragonite or calcite is thermodynamically favored. When  $\Omega < 1$ , seawater is undersaturated and dissolution of aragonite or calcite is thermodynamically favored. If  $\Omega = 1$ , the  $\text{CaCO}_3$  in the seawater is in equilibrium. The depth at which  $\Omega = 1$  is called the saturation horizon. Laboratory experiments have shown that deep-sea corals calcify slower as saturation state of aragonite ( $\Omega_{\text{ar}}$ ) decreases and can experience a net dissolution of their skeletons in undersaturated water (Maier et al., 2009; Form and Riebesell, 2012; Maier et al., 2016). However, other research found that calcification did not change in response to low  $\Omega_{\text{ar}}$  (Maier et al., 2013; Form and Riebesell, 2012).

Recent observations have shown that saturation horizons have shoaled (Feely et al., 2004), meaning that deep-sea corals previously in supersaturated waters are now being exposed to undersaturation. Shallower aragonite saturation horizons (ASH) may limit biodiversity of deep sea corals (Guinotte et al. 2006, Cairns 2007) and changes in deep-sea community composition have been found near the saturation horizon (Baco, 2007; Thresher et al., 2011). In the Northwestern Hawaiian Islands, calcifying deep-sea corals have been found below 3000 m depth in water undersaturated with  $\text{CaCO}_3$  (Baco, 2007). Currently it is not understood how deep-sea corals calcify in or will adapt to undersaturated waters as saturation horizons shoal. There is also concern that the impact of OA on calcareous microplankton could affect the food supply to benthic communities and filter-feeding deep-sea corals (Guinotte et al., 2006).

### **Deep-sea Corals in the North Pacific**

The deep waters of the North Pacific originate from influxes from the South Pacific (Reid, 1997). The water moves northward across the equator in the west and then circulates east. The

Hawaiian Islands serve as a barrier between two gyres in the intermediate waters (800-1000 m depth): the anticyclonic gyre south of 25°N and the cyclonic gyre north of 35°N (Reid, 1997). Phosphate ( $\text{PO}_4^{3-}$ ) and nitrate ( $\text{NO}_3^-$ ) concentrations are approximately 0.25 and 2  $\mu\text{mol kg}^{-1}$ , respectively, at the surface in the region of the Hawaiian Archipelago, and silica concentrations decrease in higher latitudes (Reid, 1997). Nutrient levels in the surface waters impact phytoplankton blooms, which eventually fall into the deep waters and become a food source for deep-sea corals. However, there is not a seasonal phytoplankton bloom that occurs in the Hawaiian Archipelago, as does in the north Atlantic.

Waters of the North Pacific and around the Hawaiian archipelago have a shallow ASH compared to the rest of the world's oceans, ranging from 50-600 m (Feely et al., 2004; Guinotte et al., 2006). This is likely due to the accumulation of  $\text{CO}_2$  in the Pacific's deep waters. Feely et al. (2012) found that between 1991 and 2006 the  $\Omega_{\text{ar}}$  in waters 0-1500 m depth had decreased by almost 16%. Decreases in the  $\Omega_{\text{ar}}$  were also found to occur deeper in the western Pacific than the eastern Pacific, which is probably due to the larger intake of  $\text{CO}_2$  by the western Pacific (Sabine et al., 2008). Guinotte et al. (2006) noted that there was little coral rubble in the North Pacific to provide the foundation for a reef structure, but solitary corals could survive close to the ASH by counteracting the inhospitable seawater chemistry with physiological mechanisms. Calcifying organisms, like octocorals (Figure 1), that use the most stable form of  $\text{CaCO}_3$ , calcite, tend to dominate North Pacific benthic communities (Baco, 2007; Guinotte et al., 2006), although deep-sea corals have been documented well below the ASH at 3000 m (Baco, 2007). In addition, scleractinian reefs have recently been discovered on seamounts in the Northwestern Hawaiian Archipelago (Rogers et al., 2007; Baco, *personal communication*). This directly contrasts with the bulk of literature noting the relative absence of scleractinians due to the shallow ASH (Guinotte et

al., 2006; Roberts et al., 2006). Regardless, the seamounts of the Northwestern Hawaiian Archipelago are considered a hotspot for highly diverse deep-sea coral communities (Baco, 2007).

### **Research Objectives**

Little research has been done to assess OA's effect on calcareous deep-sea corals even though these support diverse ecosystems that are crucial to fisheries worldwide (Roberts et al., 2006; Baco, 2007). In fact, the carbonate chemistry, oxygen, and nutrient conditions of the waters surrounding deep-sea corals, and the variability in water chemistry on different time scales, has not been well characterized. This study focuses on characterizing the seawater carbonate chemistry near deep-sea corals, determining the depth of the calcite saturation horizon (CSH) and ASH from 2014 to 2015, and comparing today's CSH and ASH depths to that of the 1990s to identify whether  $\text{CaCO}_3$  saturation horizons have shoaled in the last few decades in the North Pacific in the Northwestern Hawaiian Islands.

## CHAPTER II

### METHODS

#### Data Collection and Sample Analysis

Data from recent and historical measurements of dissolved inorganic carbon (DIC), total alkalinity (TA), dissolved oxygen (DO), and concentrations of the inorganic nutrients  $\text{NO}_3^-$ ,  $\text{PO}_4^{3-}$  and silicate ( $\text{SiO}_4^{2-}$ ) were examined. Historical data were collected from the World Ocean Circulation Experiment (WOCE) from 1993 and 1994 and recent data were collected from two cruises conducted in November 2014 and October 2015 (Figure 2). The 2014 and 2015 seawater samples were analyzed for TA and DIC by a Versatile INstrument for the Determination of Total inorganic carbon and titration Alkalinity (VINDTA). DIC and TA values from the VINDTA analysis were standardized using certified reference materials (CRMs; Dickson, 2001; Dickson et al., 2007) and an adjusted coulometer blank that reflects the average blank of the day the samples were processed.

DIC represents the summation of the concentrations of inorganic carbon dissolved into seawater:  $\text{CO}_2$ ,  $\text{H}_2\text{CO}_3$ , bicarbonate ( $\text{HCO}_3^-$ ), and  $\text{CO}_3^{2-}$ . TA characterizes the buffering capacity of seawater primarily through reactions with  $\text{CO}_3^{2-}$ ,  $\text{HCO}_3^-$ , borate ( $\text{BOH}_4^-$ ), and hydroxide ( $\text{OH}^-$ ) ions. Using the Excel Workbook Visual Basic for Applications translation of the original CO2SYS program (Lewis and Wallace, 1998), the corrected DIC and TA values and in-situ salinity, temperature, and pressure were utilized to calculate pH, the partial pressure of  $\text{CO}_2$  ( $p\text{CO}_2$ ),  $\Omega_{\text{ar}}$ , and calcite saturation state ( $\Omega_{\text{ca}}$ ).

## Comparison of Past and Present Seawater Chemistry

For this study, data from WOCE sites P14N-67 from cruise 325023 and P15N-60 and P15N-62 from cruise 18DD9403 (Figure 1, green sites) were compared to two sites, Bank 11 and Pioneer Bank, where data were collected in both 2014 and 2015 (Figure 1, yellow sites). These were the only sites where data were collected in both 2014 and 2015 and were chosen to maximize the number of data points to calculate ASH and calcite saturation horizon (CSH) depths. The WOCE sites closest to the 2014/2015 sites were chosen. Calculation of the CSH and ASH were approached in two ways. For the first method, logarithmic trend lines were fit to all the data available for each time period and the logarithmic equation was used to calculate at what depth  $\Omega=1$  for the 1990s, 2014, and 2015. Secondly, average saturation states were calculated for every 100 m in depth for the 1990s, 2014, and 2015 data. Data that fell just above and below  $\Omega=1$  were identified. A linear relationship between the two data points was established and the linear equation was used to calculate at what depth  $\Omega=1$ . Shoaling rates from 1993/1994 to 2014/2015 were determined by dividing the change in depth of the respective saturation horizons calculated from the logarithmic trend lines by the approximate time change, 20 years. Nutrient concentrations including  $\text{NO}_3$ ,  $\text{PO}_4^{3-}$  and  $\text{SiO}_4^{2-}$  were also compared from the 1990s to the 2010s.

## CHAPTER III

### RESULTS

#### Carbonate Chemistry

The depth profile of saturation states of both calcite and aragonite exhibited a curved trend with the highest values found in the upper 100 m depth (Figure 3). The average  $\Omega_{ca}$  and  $\Omega_{ar}$  of every 100 m also followed this trend (Figure 4). Although data in Figure 3 appear to show a decrease in  $\Omega_{ca}$  in the upper 100 m over the last 20 years, the average  $\Omega_{ca}$  in the 1990s,  $5.45 \pm 0.72$ , is not significantly different from the 2014 or 2015 average of  $5.35 \pm 0.31$  and  $4.84 \pm 0.84$ , respectively, (T-test,  $p > 0.05$ ). There was also no significant difference in  $\Omega_{ar}$  in the upper 100 m between the 1990s data and 2014 or 2015 (T-test,  $p > 0.05$ ). Fewer samples were taken deeper in the water column, below 1000 m depth only seven samples were collected in the 1990s, three in 2014, and five in 2015. This artificially decreased the standard deviation at these depths.

CSH from the logarithmic trend lines have shoaled 117 m depth from the 1990s to 2014 and 152 m depth from the 1990s to 2015 (Table 1). However, CSH from the linear trend lines have deepened 21 m depth from the 1990s to 2014 and 57 m from the 1990s to 2015. ASH calculated from the logarithmic trend lines have shoaled 113 m depth from the 1990s to 2014 and 95 m depth from the 1990s to 2015 (Table 2). ASH from the logarithmic trend line deepened between 2014 and 2015 by 17 m; however, the ASH is deeper overall in the 1990s. In addition, ASH from the linear trend lines have shoaled 9 m depth from the 1990s to 2014 and 33 m from the 1990s to 2015.

## Nutrient Data

$\text{NO}_3^-$  concentrations between 2014 and 2015 were not significantly different and showed the same increase with depth, with concentrations from 0 to  $0.8 \mu\text{mol L}^{-1}$  in the top 100 m, increasing to a maximum of  $42.93 \mu\text{mol L}^{-1}$  at 996 m (Figure 5A).  $\text{NO}_3^-$  data was unavailable for the 1990s.  $\text{PO}_4^{3-}$  concentrations were consistent over time with no significant difference between the 1990s, 2014, and 2015 data (Figure 5B). Concentrations were below  $0.5 \mu\text{mol L}^{-1}$  in the upper 200 m depth, the euphotic zone, but increased with depth to a maximum of  $3.36 \mu\text{mol L}^{-1}$  at 1000 m.  $\text{SiO}_4^{2-}$  concentrations in the 1990s and 2015 agreed well with concentrations from 0.0 to  $0.73 \mu\text{mol L}^{-1}$  in the top 100 m, increasing to a maximum of  $156.89 \mu\text{mol L}^{-1}$  at 1607 m (Figure 5C). Notably,  $\text{SiO}_4^{2-}$  concentrations below 800 m were significantly lower in 2014 than in the 1990s and 2015 (Figure 5C; T-test,  $p < 0.05$ ).

## CHAPTER IV

### DISCUSSION

Our data indicate that the saturation horizons of both calcite and aragonite have gotten shallower from the 1990s to the 2010s. From 2014 to 2015, there is too much variability to look at changes in ASH and CSH. In fact, this study found that shoaling rates in the North Pacific are accelerating. From the preindustrial age to the 1990s, CSH were shoaling 0.21-0.51 m yr<sup>-1</sup> and ASH were shoaling 0.15-0.51 m yr<sup>-1</sup> in the North Pacific (Feely et al. 2004). From the 1990s to the 2010s, shoaling rates increased to 5.85-7.60 for CSH and 4.80-5.65 for ASH. This suggests that shoaling could be as much as 28 times faster for calcite and 32 times faster for aragonite in the last 20 years than it was from the preindustrial to the 1990s. Currently, the rate at which CO<sub>2</sub> is being emitted into the atmosphere is ten-fold the highest rate of the last 66 million years and is also accelerating (Feely et al., 2004; Zeebe, 2016). This could explain the accelerated shoaling of saturation horizons as OA and its effects are also getting faster. Changes in ocean circulation could contribute to the shoaling of the CSH and ASH as well, as water with lower saturation states could move into the region.

SiO<sub>4</sub><sup>2-</sup> concentrations below 800 m were significantly lower in 2014 than in the 1990s and 2015. This may have been caused by changes in circulation or surface primary productivity. A water mass with lower SiO<sub>4</sub><sup>2-</sup> concentrations may have moved over the seamounts or an annual diatom bloom, phytoplankton that make silicate shells or frustules, may have not been present in 2014. Lower SiO<sub>4</sub><sup>2-</sup> concentrations may also have been dependent on the El Nino/Southern Oscillation (ENSO) cycle, as it causes changes in ocean circulation and productivity throughout the Pacific Ocean (Barber et al., 1996; Corno et al., 2007). An El Nino phase occurred in 1993-

1994 and 2015, but not in 2014 when low  $\text{SiO}_4^{2-}$  concentrations were observed. Primary productivity rates in the euphotic zone (upper 200 m depth) at station ALOHA north of Oahu increased significantly during El Nino events including the 1991-1994 El Nino, although primary productivity was based on in situ  $^{14}\text{C}$  incorporation into particulate matter and did not differentiate between species (Corno et al., 2007). During the 1997-1998 El Nino event, export from diatoms and silicoflagellates, another group of microphytoplankton with a silicate shell, had diminished by 75% off the coast of Chile (Romero et al., 2001).

To conclude, our data clearly show that ASH in the Northwestern Hawaii Islands have shoaled over the last 20 years. Although not as clear, there is evidence that CSH have also shoaled. The rate at which the saturation horizons of both calcite and aragonite appears to have accelerated almost thirty-fold. Deep-sea corals on seamounts in the Northwestern Hawaiian Islands are being exposed to water undersaturated with respect to  $\text{CaCO}_3$  at shallower depths much faster than before the 1990s. Although it is not well understood how deep-sea corals are being affected by OA or undersaturation, the high  $\text{CO}_2$ , low pH conditions of the deep-sea environment could cause them to be particularly susceptible to any changes in carbonate chemistry. More investigation must be undertaken to ascertain how well deep-sea corals like those in the Northwestern Hawaiian Islands will endure these adverse circumstances. In addition, further work must be done to compare the 1990s and 2010s depth profiles to ascertain whether the difference in saturation horizons is statistically different. Additional data from the 2010s would be valuable to determine the effect of ENSO on primary productivity and nutrient concentrations and to verify the rate of saturation horizon shoaling in the Northwestern Hawaiian Islands.

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## TABLES

Table 1. Saturation horizons for calcite calculated from logarithmic and linear trend lines in Figures 2 and 3. Standard deviation for linear trend lines are averages of one standard deviation of depths just above and below  $\Omega_{ca}=1$ .

<b>Calcite</b>	Trend Lines	
	Logarithmic	Linear
1990s Saturation Horizon	1006 m	$766 \pm 0$ m
2014 Saturation Horizon	889 m	$791 \pm 27$ m
2015 Saturation Horizon	854 m	$823 \pm 23$ m

Table 2. Saturation horizons for aragonite calculated from logarithmic and linear trend lines in Figures 2 and 3. Standard deviation for linear trend lines are averages of one standard deviation of depths just above and below  $\Omega_{ca}=1$ .

<b>Aragonite</b>	Trend Lines	
	Logarithmic	Linear
1990s Saturation Horizon	747 m	$598 \pm 25$ m
2014 Saturation Horizon	634 m	$589 \pm 41$ m
2015 Saturation Horizon	652 m	$565 \pm 47$ m

## FIGURES

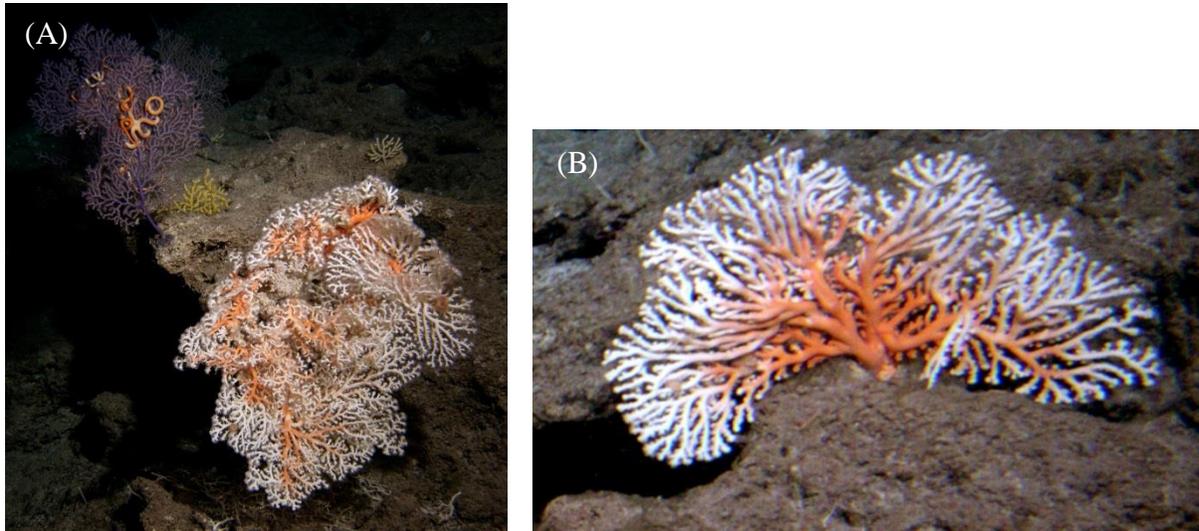


Figure 1(A). A collection of deep-sea corals including *Corallium secundum* (foreground), an acanthogorgiid octocoral (middle), and an unidentified octocoral (background) found in the Northwestern Hawaiian Islands. (B) A “pink coral”, *C. secundum*. (Both images from Baco et al. 2007).

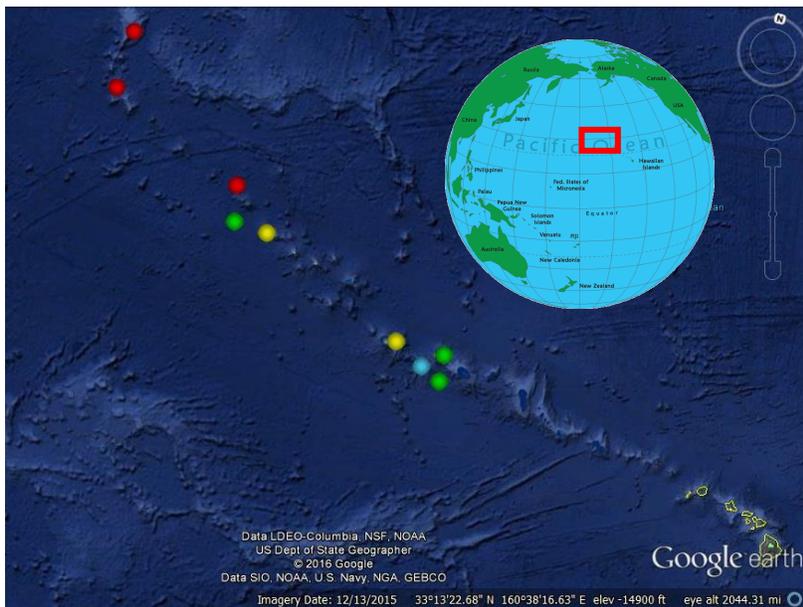


Figure 2. Locations of sample sites: 1993 and 1994 in green, 2014 in blue, 2015 in red, and 2014 and 2015 in yellow. Sites from the 1990s (green) were compared to sites from both 2014 and 2015 (yellow) due to proximity to determine if saturation horizons were shoaling.

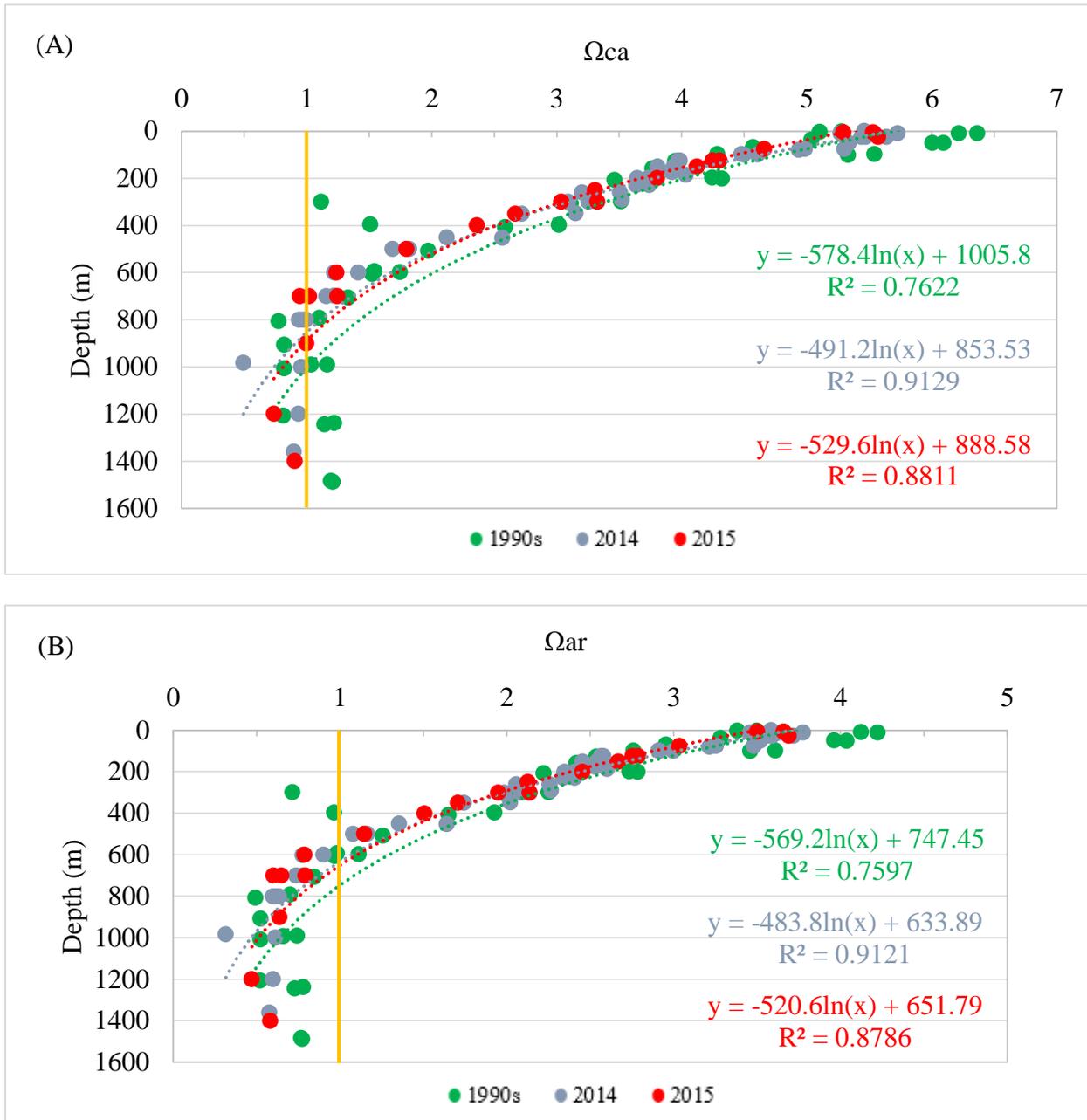


Figure 3(A and B). Logarithmic trend lines fit on raw  $\Omega_{ca}$  and  $\Omega_{ar}$  data to identify the saturation horizon ( $\Omega=1$ ). Data, logarithmic trend line, and logarithmic trend line equation (bottom right) for 1990s is shown in green, for 2014 in blue, and for 2015 in red. The saturation horizon is marked by an orange line.

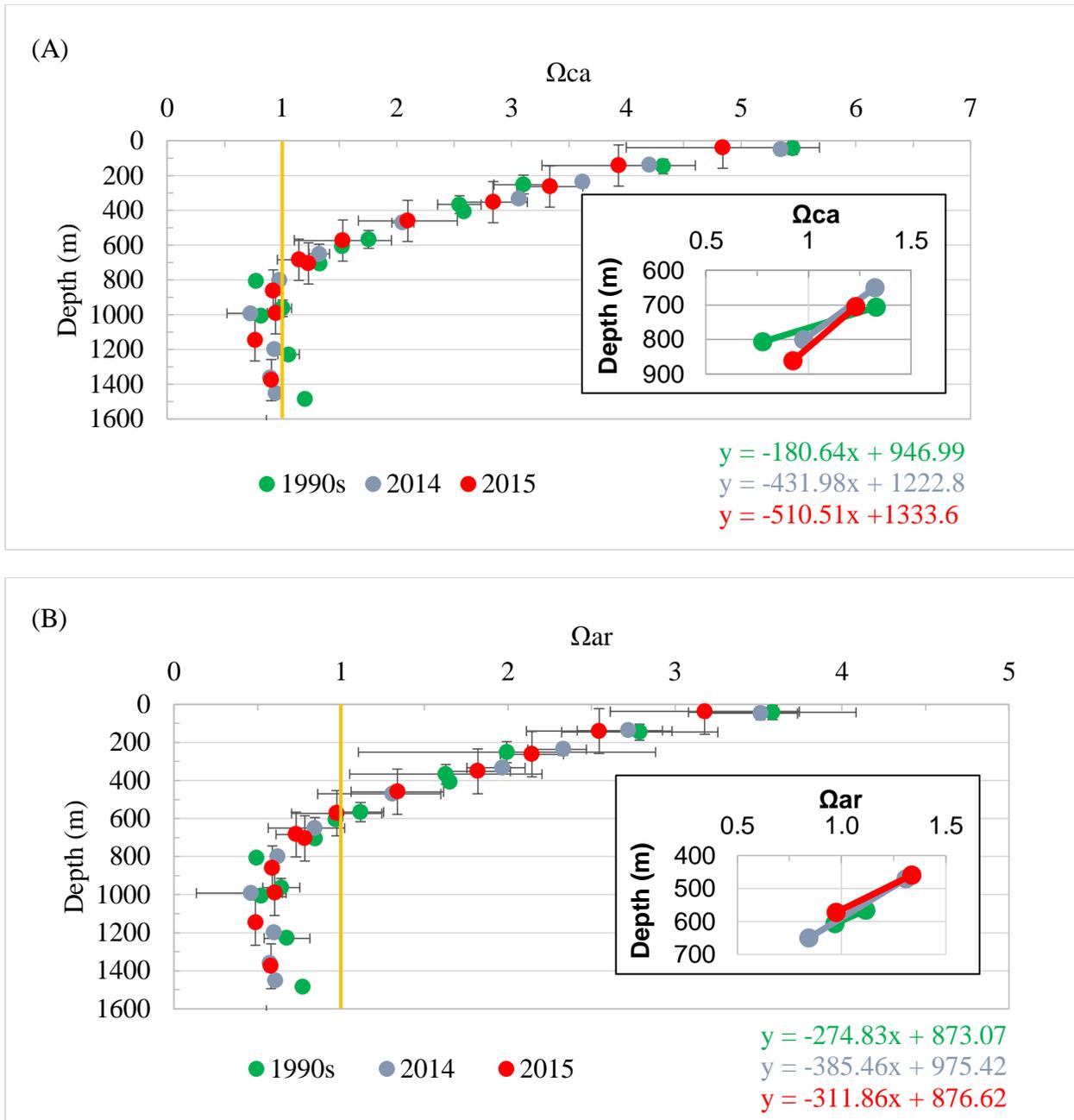


Figure 4(A and B). Average  $\Omega_{ca}$  and  $\Omega_{ar}$  of every 100 m with standard deviation. To calculate the saturation horizon, the depths directly before and after  $\Omega=1$  were fit to a linear trend line (inset graph). Data, logarithmic trend line, and logarithmic trend line equation (bottom right) for 1990s is shown in green, for 2014 in blue, and for 2015 in red. The saturation horizon is marked by an orange line.

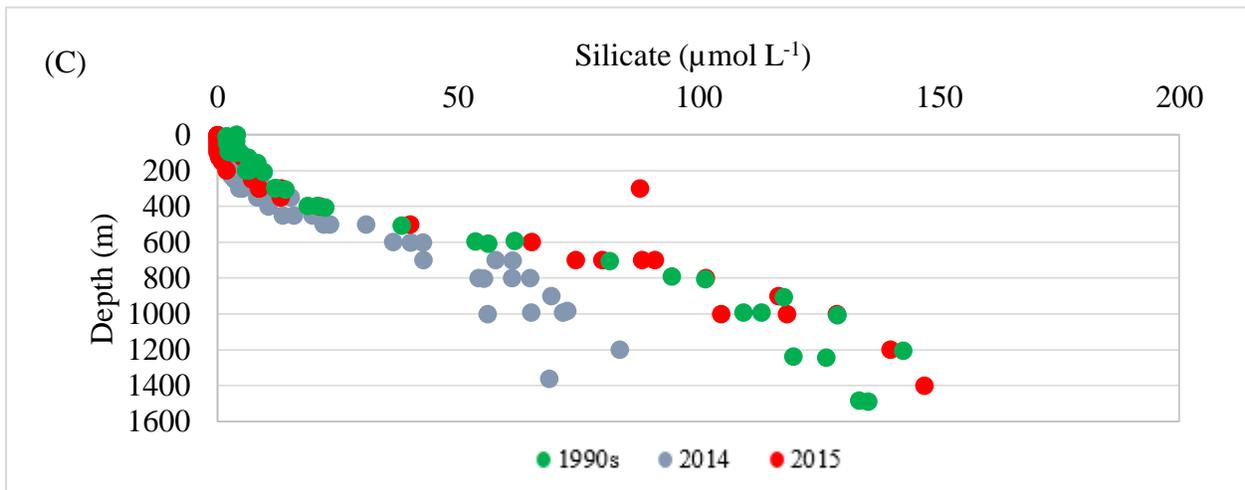
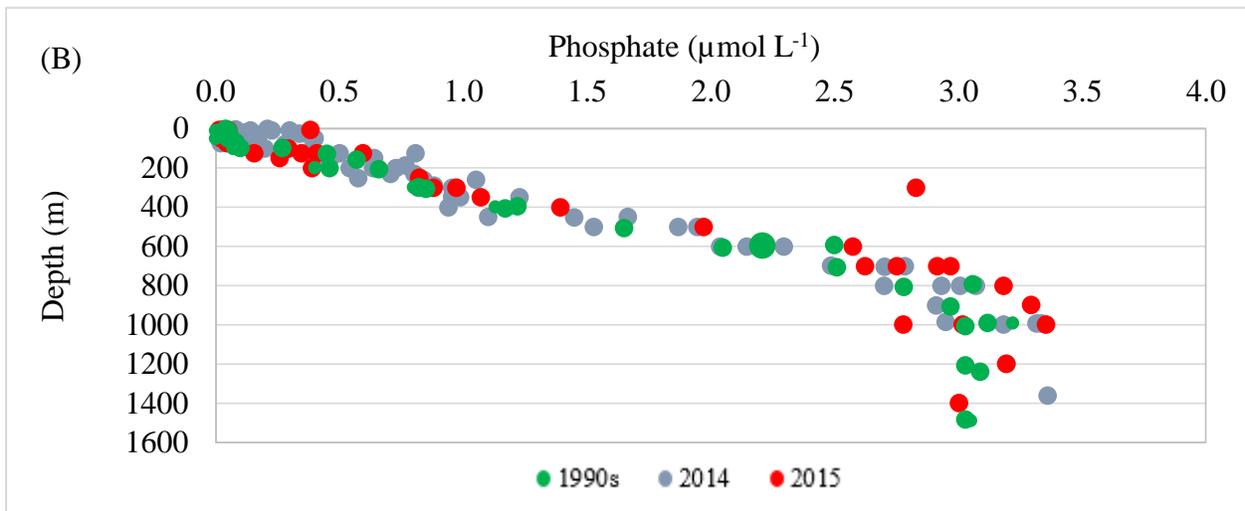
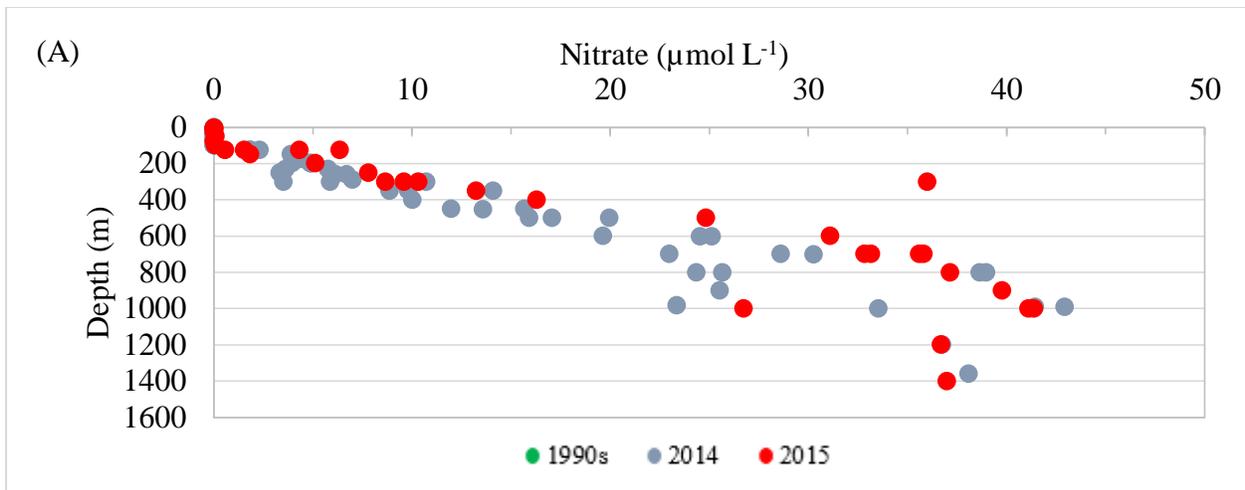


Figure 5(A). Nitrate concentrations, (B) phosphate concentrations, and (C) silicate concentrations from the 1990s (green), 2014 (blue), and 2015 (red).