Southern Ocean Acidification: Assessing Vulnerability

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ABSTRACT

Models project that with current CO_2 emission rates the Southern Ocean surface will be undersaturated with respect to aragonite and calcite by the end of the 21st century resulting in widespread impacts on biogeochemistry and the ocean ecosystem. However, accurate assessment of future acidification changes and impacts require a better understanding of present-day saturation state and depth of the saturation horizon in the Southern Ocean. We analyze present-day carbonate chemistry and assess the current vulnerability of the Southern Ocean with respect to ocean acidification using freely-available cruise data published in the Global Ocean Data Analysis Project Version 2 (GLODAPv2), along with an interpolated version of these data that gap fills when data have not been collected at a particular location or time. We find that the present-day saturation horizon for aragonite varies from 400-2000 m depth. The aragonite saturation horizon is shallowest around 60°S and deeper North and South of this latitude at 40°S and 70°S. The Calcite saturation horizon is shallowest in the South Pacific and along 60°S. We find very low data density at the depth of the saturation horizon, which may bias the interpolated product's estimate of the horizon depth in many locations. We further assess whether predictions of the present-day horizon depth from Earth system models are consistent with these observations.

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1. Introduction

Rising atmospheric carbon dioxide (CO_2) levels resulting from fossil fuel emissions and industrial and agricultural activities have been abated by oceanic uptake, which has absorbed nearly a third of the total anthropogenic carbon added to the atmosphere (Feely et al. 2004). As the ocean absorbs atmospheric CO_2, unstable carbonic acid (H_2CO_3) is formed and then dissociates to create bicarbonate (HCO_3^-) and hydrogen ions (H^+). The increase in hydrogen ions decreases the pH, therefore increasing ocean acidity (Doney et al. 2009).

Ocean acidification is also associated with a decrease in the carbonate ion concentration ($[CO_3^{2-}]$), which decreases the saturation state ($\Omega = [Ca^+][CO_3^{2-}]/K_{sp}$) of calcium carbonate ($CaCO_3$) minerals aragonite and calcite. Ω_{Ar} and Ω_{Ca} are defined as the ratio of the concentration of dissolved ions currently present in a given solution to the concentration of dissolved ions in a saturated solution of aragonite and calcite, respectively. Aragonite and calcite chemically dissolve once Ω decreases below the well-established thermodynamic threshold of 1, which is where the saturation horizon occurs, and where waters are considered undersaturated (Hauri et al. 2015). Below the saturation horizon, it is difficult for marine calcifying organisms (e.g. coral, phytoplankton, or foraminifera) to form biogenic calcium carbonate which they require to build their shells (Orr et al. 2005; Hauri et al. 2015; Doney et al. 2009).

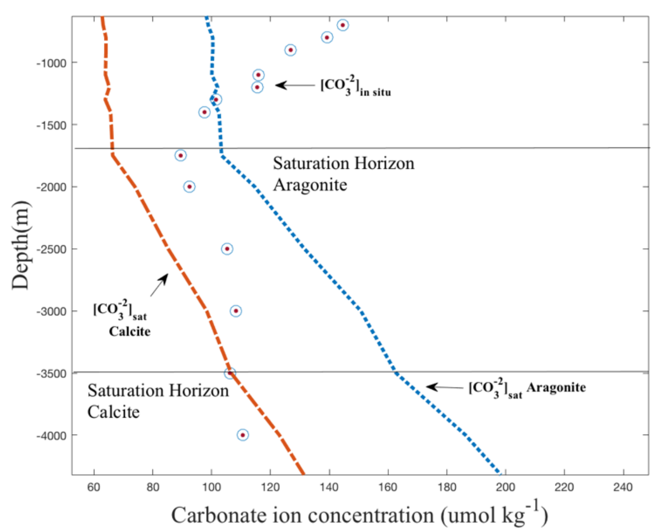

Figure 1. Illustration of the calcite and aragonite saturation horizon in the Southern Ocean using Cruise WOCE 1994. As pressure increases with depth, the saturation concentration of calcite and aragonite increases as well ($[CO_3^{2-}]_{sat}$). The crossover between the in situ carbonate ion concentration and the saturation concentration for calcite and aragonite determines the saturation horizon of the different mineral phases.

The Southern Ocean, which we define as all longitudes south of 40°S, is especially vulnerable to the effects of acidification relative to lower latitudes due to colder temperatures, which increase the solubility of CO_2 in the water column, as well as surface winds causing upwelling of deep sea water, which contains high CO_2 concentrations from organic matter remineralization (Doney et al. 2009; Fabry et al. 2009; Orr et al. 2005). With current CO_2 emission rates, models project that the Southern Ocean surface will be undersaturated with respect to aragonite and calcite by the end of the 21st century (Feely et al. 2004; Orr et al. 2005; Hauri et al. 2015). This suggests that key marine calcifying organisms, such as those listed above, will have difficulty maintaining or building external calcium carbonate skeletons (Orr et al. 2005). The inability for marine organisms to build their shells will limit aragonitic organisms as well as change the food web dynamics and potentially have cascading effects on both global ocean and terrestrial ecosystems (Doney et al. 2009). If model projections of changes in pH in the Southern Ocean are accurate, ecosystem impacts in the Southern Ocean will serve as a bellwether for prospective impacts of ocean acidification on marine organisms at mid and low latitudes where ocean acidification is projected to occur more slowly (Fabry et al. 2009).

Accurate assessment of future acidification changes and impacts requires a better understanding of present-day saturation state and depth of the saturation horizon in the Southern Ocean. Due to the remoteness and the rough conditions of the Southern Ocean, it has been difficult to obtain observations. The few available in-situ observations likely contain a seasonal summer bias due to the difficulty of sampling during the winter, yet it is important to thoroughly analyze all available data. This study analyzes freely available hydrographic observations of Southern Ocean carbonate chemistry, using three formats of Global Ocean Analysis Project Version 2 (GLODAPv2) carbonate data: original individual cruise data, merged cruise data, and an interpolated "mapped climatologies" dataset (Key et al. 2015; Lauvset et al. 2016; Olsen et al. 2016). While these data are available globally, this analysis focuses only on the Southern Ocean (all longitudes south of 40°S). The analysis focuses on the saturation state and the saturation horizon of both Aragonite and Calcite to understand whether and how the vertical distribution of carbonate ion concentration varies from place to place in order to assess the trustworthiness of the interpolated dataset given the data density. This analysis will allow us to better verify and improve model simulations to provide a better prediction of acidification in the Southern Ocean. This paper is organized the following way: Section 2 describes the data and methods in detail, Section 3 describes results, and Section 4 concludes and discusses results.

2. Methods

2a. Data Analysis

This analysis uses Global Ocean Data Analysis Project Version 2 (GLODAPv2) observations in three different structures; the original, unadjusted individual cruise data, a merged and internally consistent data product, and an interpolated mapped climatology (Key et al. 2015; Lauvset et al. 2016; Olsen et al. 2016). The data resulted from approximately one million individual seawater samples collected from over 724 cruises during the years 1972-2013 (Key et al., 2015). A majority of the observations were received from data centers associated with the WOCE, OACES, and JGOFS research programs (Sabine et al. 2005). The Southern Ocean (South of 40°S, and circling Antarctica) was the primary area analyzed in this study.

2b. GLODAPv2 Cruise Data

All the cruises included measurements of pressure, temperature, salinity, oxygen and nutrients. For the majority of the samples, pressure and temperature data were obtained from CTD measurements, while salinity and nutrient samples were obtained from individual Niskin-type bottles collected with a Rosette (Sabine et al. 2005).

All TCO_2 measurements were analyzed by coulomertic titration, while total alkalinity measurements were obtained by potentiometric titration using a titrator and a potentiometer (Sabine et al. 2005). In cruises where total alkalinity was not measured, it was calculated from

TCO_2 and whatever second parameter was measured and reported in the GLODAP database (Sabine et al. 2005).

This compiled and adjusted data product is believed to be consistent to better than 0.005 in salinity, 1% in oxygen, 2% in nitrate, 2% in silicate, 2% in phosphate, 4 $\mu mol\ kg^{-1}$ in dissolved inorganic carbon, 6 $\mu mol\ kg^{-1}$ in total alkalinity, and 0.005 in pH (Olsen et al. 2016).

For more details on data collection methods used to gather the carbonate data or any of the measurements, see the *Sabine et al*. 2005 data construction section or (http://cdiac.ornl.gov/oceans/GLODAPv2/cruise_table.html) which contains a table with the documentation of each of the cruises.

2c. "Mapped Climatology" Interpolated Dataset

The quality-controlled GLODAPv2 merged data set was used to create global mapped climatologies using the Data-Interpolating Variational Analysis (DIVA) mapping method (Lauvset et al. 2016). The "mapped climatologies" data set was created by interpolating the discrete data onto the depth surfaces and normalizing it to the year 2002 by removing the temporal trends in TCO_2 and pH due to anthropogenic influence (Lauvset et al. 2016).

To ensure that as many carbon data as possible were accompanied by supporting biochemical data, missing salinity, oxygen, nitrate, and phosphate values were vertically interpolated in the Southern Ocean using a quasi-Hermetian piecewise polynomial that was then evaluated at 33 surfaces (Sabine et al. 2005; Lauvset et al. 2016). Interpolation was used when vertical data separation distances were within 25 meters in the top 100 meters, within 75m between 101-300m, within 150m between 301-750m, within 505m between 751-2000m, and within 1005m between 2001m to the bottom (Key et al. 2009). The vertical interpolated data for each depth surface where then gridded by bin-averaging in each 1° by 1° grid cell (Lauvset et al. 2016).

Aragonite and calcite saturation were calculated from DIC 2002 and total alkalinity pairs at in situ temperature and pressure, while pH was calculated from DIC 2002 and total alkalinity pairs at both in situ temperature and pressure and at constant temperature and pressure (Lauvset et al. 2016).

Biochemical measurements in the Southern Ocean contain a seasonal bias, since it is almost exclusively sampled during the austral summer (December - March) due to prohibitive wintertime weather. No attempt has been made to correct for this seasonal bias due to limited data coverage, and such correlations would have to rely on relationships with ancillary variables and different temporal gap-filling methods (Lauvset et al. 2016).

2d. Carbonate Data

We calculated the full carbonate system from individual cruises using temperature, salinity, total alkalinity and DIC as parameters for the program CO2SYS (Lewis et al. 1998).Total alkalinity and TCO_2 were used instead of pH or fCO_2 because they are conservative variables that are not affected by temperature and pressure (Sabine et al. 2005).

3. Results and Discussion

3a. "Mapped Climatology" Interpolated Dataset

As a result of both hydrostatic pressure and lower temperature, aragonite and calcite saturation state (Ω_{Ar} and Ω_{Ca}) diminishes with depth and reaches a distinct "saturation horizon" below which waters become under-saturated for both aragonite and calcite (Figure 1; Jiang et al. 2015). The "Mapped Climatologies" interpolated dataset was used to evaluate the saturation state and depth of the saturation horizon of aragonite and calcite in the Southern Ocean, and the depth of the saturation horizon was identified as the depth where aragonite or calcite saturation is less than one but greater than 0.9.

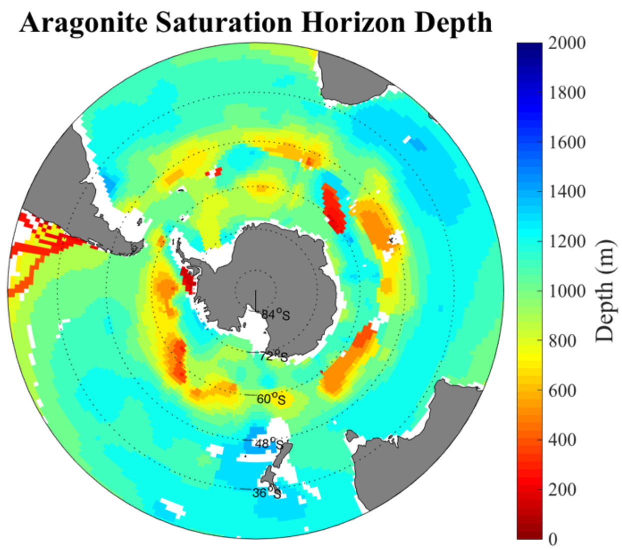

Figure 2. Aragonite saturation horizon depth (m) in the Southern Ocean using the "Mapped Climatologies" interpolated dataset published by GLODAPv2.

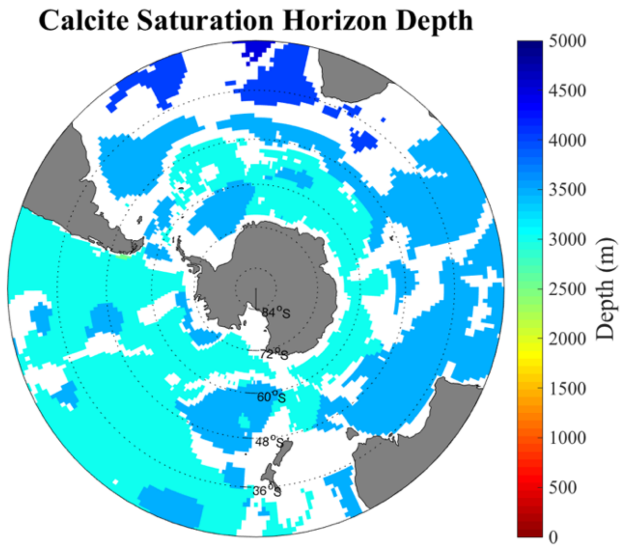

Figure 3. Calcite saturation horizon depth (m) in the Southern Ocean using the "Mapped Climatologies" interpolated dataset published by GLODAPv2. White indicates the saturation horizon depth is coincident with the bottom of the Ocean.

Figure 2 suggests that the shallowest aragonite saturation horizon depth (~ 200 meters; red) is between 50°S and 60°S in all basins of the Southern Ocean. There is also a region of shallow aragonite horizon depth off the coast of Chile. The deepest aragonite saturation horizon depths (~ 1400 meters; light blue) occur in the southwestern Indian Ocean, as well as east of Argentina and around New Zealand. The depth of the calcite saturation horizon is significantly deeper than that of the aragonite saturation horizon. As seen on Figure 3, the saturation depth for calcite ranges from 5000 to 3000 meters and has the shallowest saturation horizon along the Pacific Ocean and along 60°S.

To get a sense of how the GLODAP interpolation scheme may bias our interpretation of saturation horizon depth, we mapped the number of observations collected at the saturation horizon depth in each grid cell (Figures 4 and 5). Very few grids cells contain observations at the depth of the saturation horizon for either aragonite or calcite, and if observations are present they average 1-2 observations. The observations are concentrated along cruise tracks and a few points have up to 10 observations at the depth horizon. Worryingly, the regions with the shallowest aragonite saturation horizon depths (Figure 2; red) have few observations to support the interpolated values.

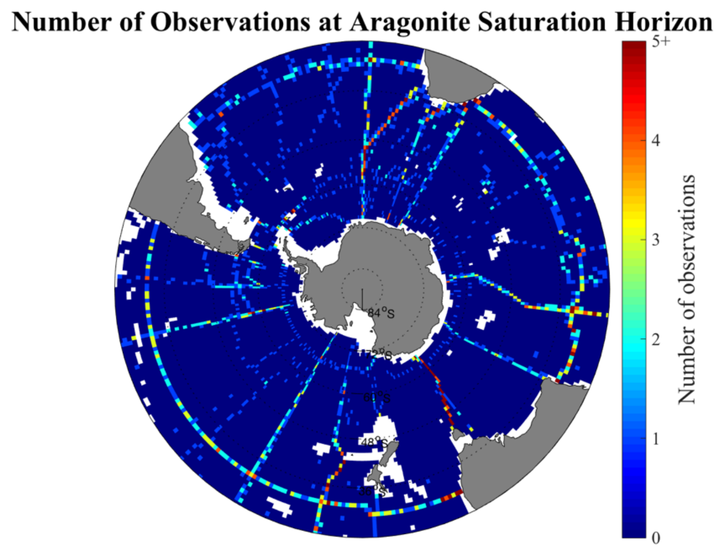

Figure 4. Number of observations at the aragonite saturation horizon depth along the Southern Ocean.

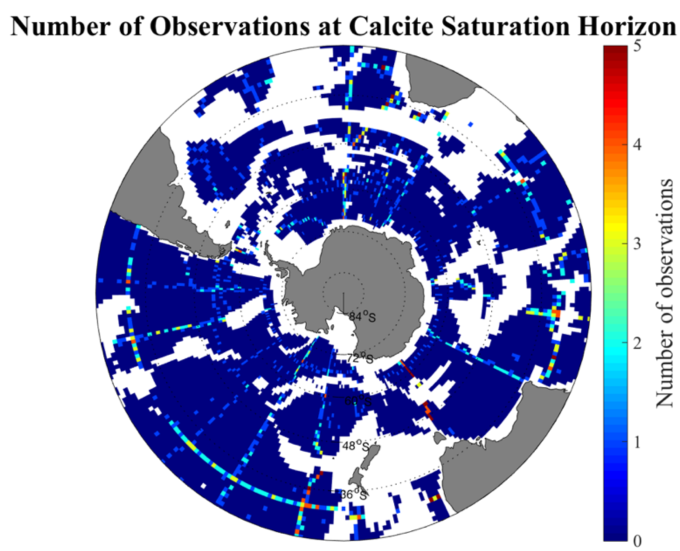

Figure 5. Number of observations at the calcite saturation horizon along the Southern Ocean.

Figures 6 and 7 show the saturation horizon depth for aragonite and calcite at only the grid cells that contain one or more observations at the saturation horizon throughout the Southern Ocean. At these grid cells with data, most points contain 1 observation and only 1.7% of grid points have more than 5 of observations. The low data density at the depth of the saturation horizon may bias the estimate of the horizon depth from the "Mapped Climatologies" interpolated product in many locations. Using the aragonite saturation horizon depths of just locations that contain observations (Figure 6), we find that the present-day saturation horizon for aragonite varies from 400-2000 m depth. The saturation horizon is shallowest around 60°S and deeper both North and South of this latitude at 40°S and 70°S. Note that many of the regions with extremely shallow aragonite horizons in the "Mapped Climatologies" interpolated data set (indicated by a strong red color in Figure 1) regions devoid of observations at the horizon. Similarly, the calcite saturation horizon depths of locations that contain observations (Figure 7) indicate that the present-day saturation horizon for calcite varies from 3000-5000 m depth, with shallower saturation horizons in the Pacific sector of the Southern Ocean, and south of 60°S.

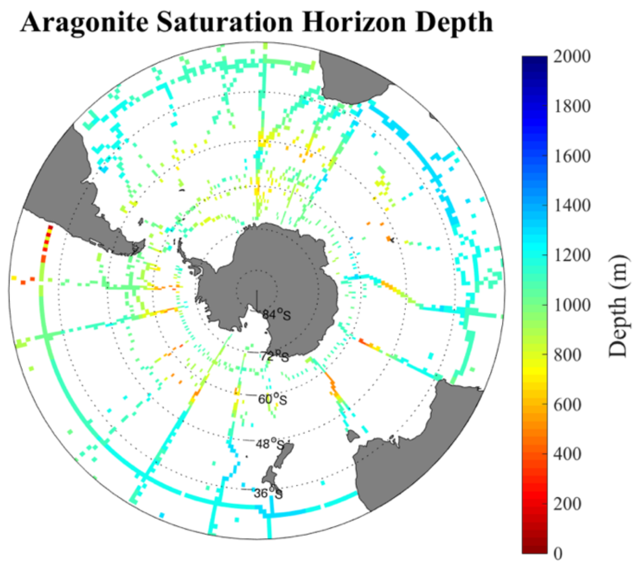

Figure 6. Depth of aragonite saturation horizon in locations that contain observations at the saturation horizon.

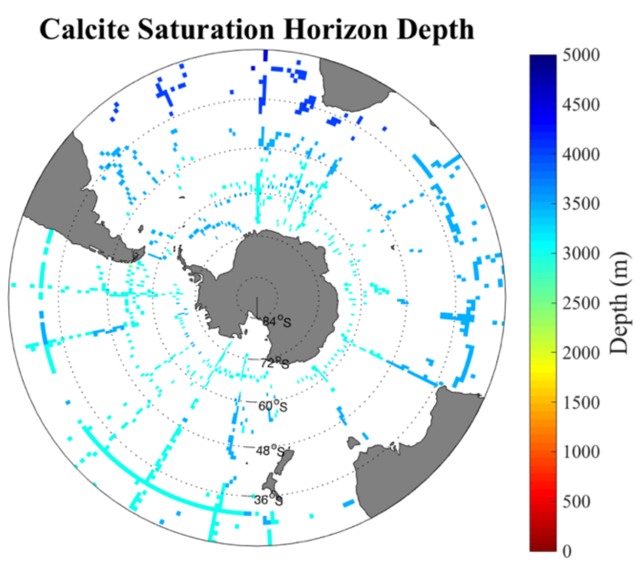

Figure 7. Depth of calcite saturation horizon in locations that contain observations at the saturation horizon.

To understand why the saturation horizon along 60°S is shallower than the waters north and south of this latitude, we analyzed vertical transect data from several cruises between Tasmania and Antarctica. This cruise track was chosen for further analysis due to the presence of a shallow horizon around 50-60°S and the relatively high data density at the depth of the horizon here. Figures 8 and 9 show the vertical transects of Dissolved Inorganic Carbon (DIC) and pH, respectively, from observations collected along this track in 1994. From north to south, we observed a shoaling of the surfaces of constant DIC and pH. The upwelling of deep sea water, which contains high CO_2 concentrations from organic matter remineralization, leads to elevated concentrations of DIC and low pH in the top 500 m between about 50-60°S. These latitudes are therefore associated with shallow aragonite saturation horizon depths.

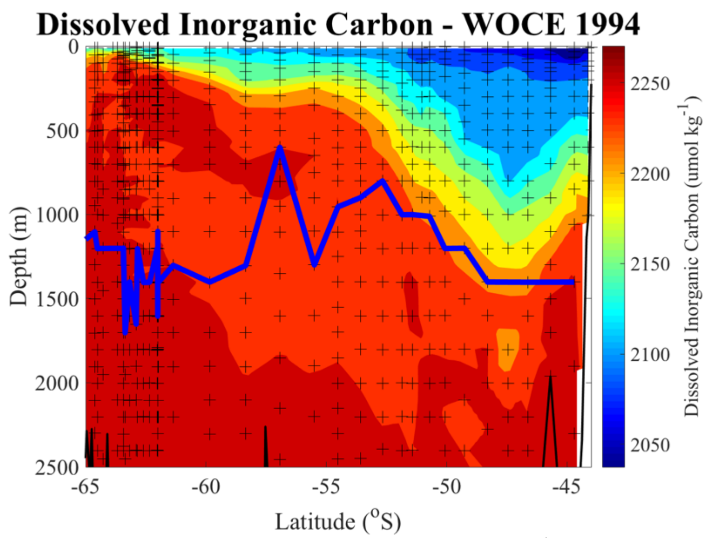

Figure 8. Zonal cross section of dissolved inorganic carbon (μmol kg^{-1}) along the WOCE 1994 ship track from Tasmania to Antarctica (Tilbrook et al. 1994). Blue line corresponds to the aragonite saturation horizon depth along the cruise path.

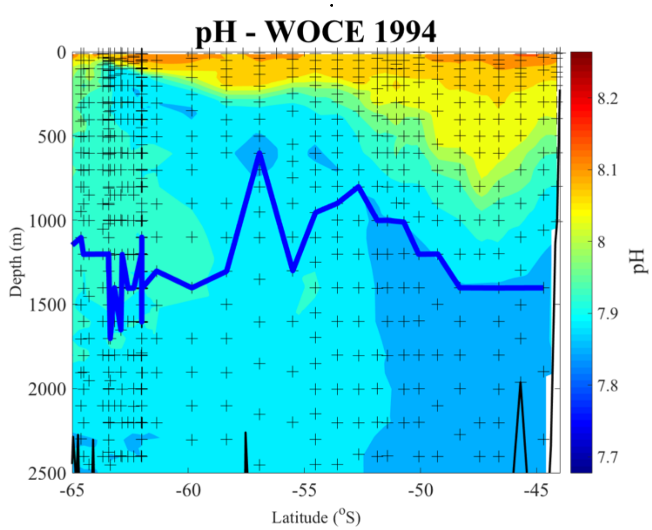

Figure 9. Zonal cross section of along the WOCE 1994 ship track from Tasmania to Antarctica (Tilbrook et al. 1994). Blue line corresponds to the aragonite saturation horizon depth along the cruise path.

3b. Seasonal Bias

Seasonal measurement bias is one of the largest sources of uncertainty for the Ω_{Ar} and Ω_{Ca} estimates in the "Mapped Climatologies" Interpolated Dataset. Seasonal variations of temperature, surface mixed layer depth, and spring blooms have a noticeable impact on Ω_{Ar} and Ω_{Ca} in some regions of the global oceans (Jiang et al. 2015). Due to the sampling logistics of the repeat hydrography cruises, very few grid points have data from all seasons. When data are available from all seasons, they are often collected many years apart, and these interannual variations challenge our ability to identify true seasonal variability.

3c. Interpolation Bias

We compare the saturation horizon depth from the "Mapped Climatology" interpolated dataset to the depth from co-located individual cruise data in Figures 10 and 11. For aragonite and calcite, the depth of the saturation horizon (Figure 10 and 11) in the majority of the Southern Ocean is shallower in the "Mapped Climatology" interpolated dataset than the individual cruise data sets. The underestimation of the saturation horizon depth should therefore be considered when using the interpolated data.

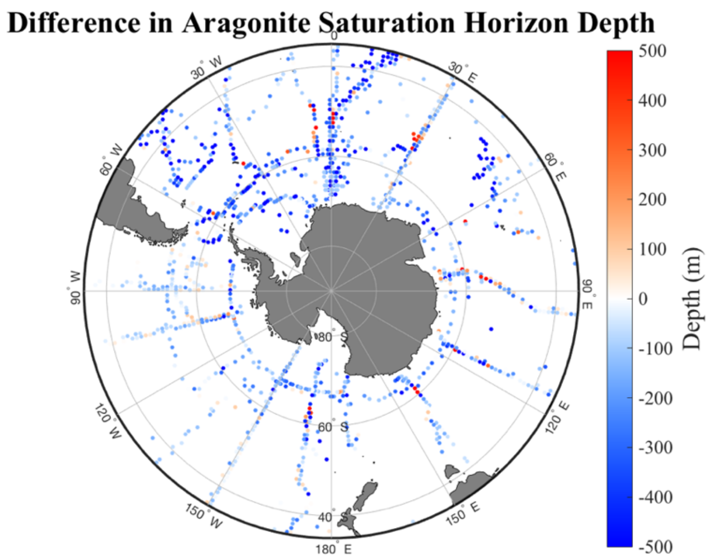

Figure 10. Difference between the "Mapped Climatology" dataset and the individual Cruise Data (MCDI- cruise), where red shows the "Mapped Climatology" dataset has deeper depths for the Aragonite Saturation Horizon at that grid cell, and blue means the Aragonite Saturation Horizon depths in the Interpolated data set are shallower.

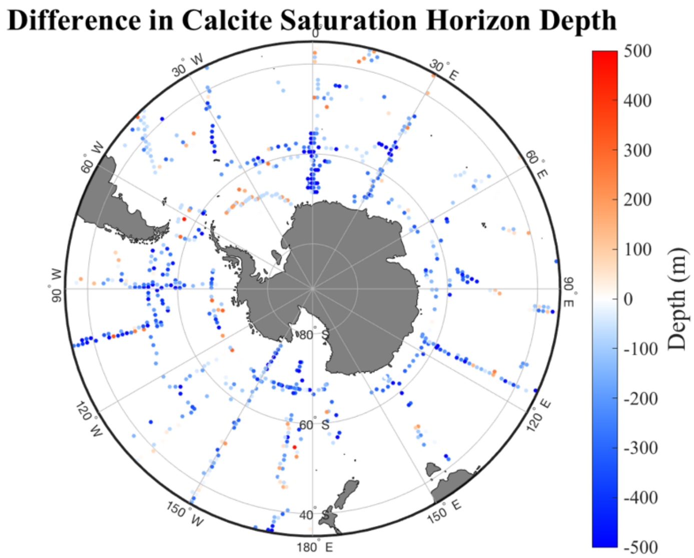

Figure 11. Difference between the "Mapped Climatology" dataset and the individual Cruise Data (MCDI-cruise), where red shows the "Mapped Climatology" dataset has deeper depths for the Calcite Saturation Horizon at that grid cell, and blue means the Aragonite Saturation Horizon depths in the Interpolated data set are shallower.

3d. Comparison with Earth System Models

We further assessed whether predictions of the present-day horizon depth from the Community Earth System Model (CESM), the Hadley Centre climate model and the Earth System Model by the Geophysical Fluid Dynamics Laboratory (GFDL) are consistent with these observations (Figures 12-14).

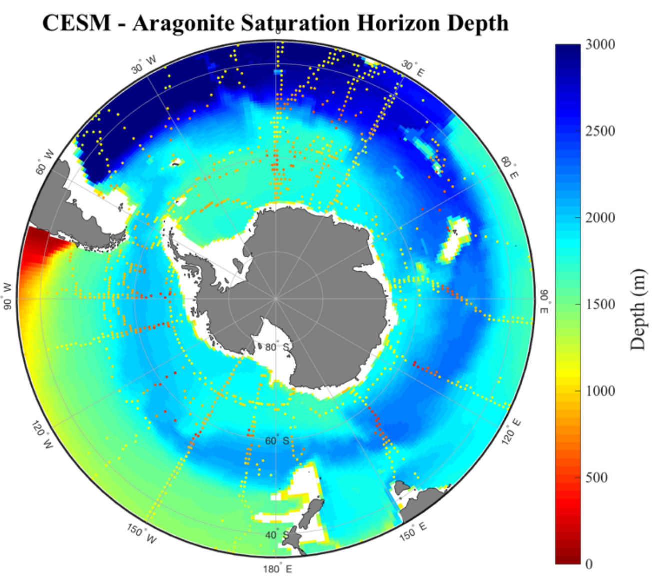

Figure 12. Comparison between GLODAPv2 Cruise Data Aragonite Saturation Horizon Depth normalized to 2002 and CESM 2002 model prediction.

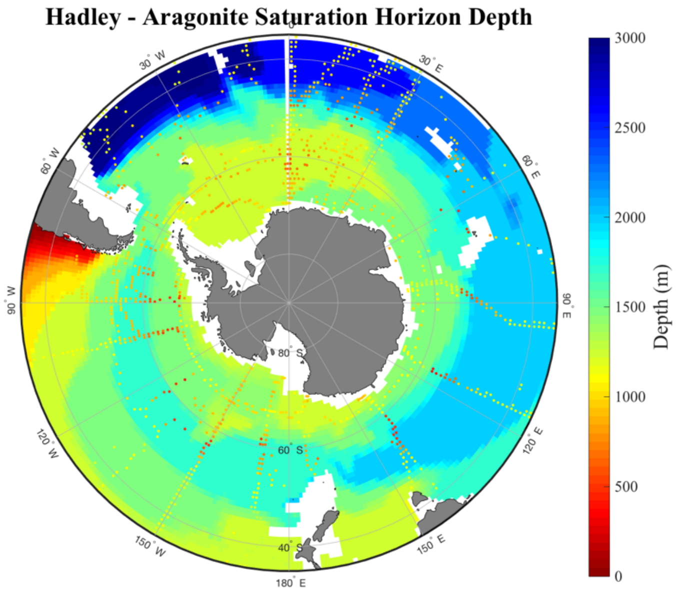

Figure 13. Comparison between GLODAPv2 Cruise Data Aragonite Saturation Horizon Depth normalized to 2002 and Hadley Centre 2002 model prediction.

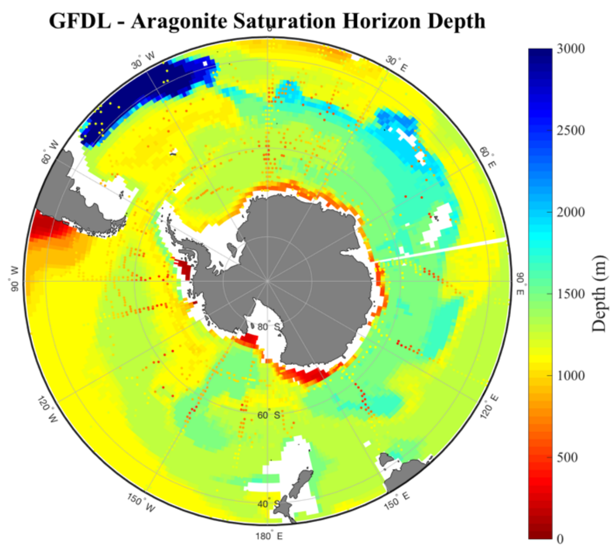

Figure 14. F Comparison between GLODAPv2 Cruise Data Aragonite Saturation Horizon Depth Normalized to 2002 and GFDL 2002 model prediction.

Our analysis reveals that each of these models has a deeper present-day aragonite saturation horizon than observed. While the models show a shallower horizon near the Antarctic continent, they also predict a deep horizon at the exact latitudes (50-60°S) where the observations indicate that the horizon is at its shallowest depth in the Southern Ocean. We suspect that these models have low DIC biases at depth, causing the mismatch between models and observations here. We note that these same models are used to make projections of the future, and a previous study using these models project that the aragonite saturation horizon will be at the surface of the Southern Ocean by the end of the century (Hauri et al. 2015). Our analysis indicates that the models have a deeper horizon than observed in the present day, and worryingly suggests that the horizon may shoal to the Southern Ocean surface well before the end of the century.

4. Conclusion

In this study, we assessed the present-day vulnerability of the Southern Ocean with respect to acidification using carbonate chemistry observations collected on repeat hydrographic cruises. We further compared these results to estimates of present day carbonate chemistry from Earth System Models. By analyzing the regions that contain observations in the “mapped climatology” interpolated data set, we find that the present-day saturation horizon for aragonite varies from 400-2000 m depth. The aragonite saturation horizon is shallowest around 60°S and deeper North and South of this latitude at 40°S and 70°S. The calcite saturation horizon is shallowest in the South Pacific and along 60°S, which could be due to the upwelling of deep water rich in carbon dioxide to the surface. We find very low data density at the depth of the saturation horizon, which may bias the interpolated product’s estimate of the horizon depth in many locations. We find that Earth System Models consistently show a deeper aragonite saturation horizon depth than observed throughout the present-day Southern Ocean. This calls into question future projections made from these models.

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