

# The role of ocean acidification in systemic carbonate mineral suppression in the Bering Sea

Jeremy T. Mathis,<sup>1</sup> Jessica N. Cross,<sup>1</sup> and Nicholas R. Bates<sup>2</sup>

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[1] Ocean acidification driven by absorption of anthropogenic carbon dioxide (CO<sub>2</sub>) from the atmosphere is now recognized as a systemic, global process that could threaten diverse marine ecosystems and a number of commercially important species. The change in calcium carbonate (CaCO<sub>3</sub>) mineral saturation states ( $\Omega$ ) brought on by the reduction of seawater pH is most pronounced in high latitude regions where unique biogeochemical processes create an environment more susceptible to the suppression of  $\Omega$  values for aragonite and calcite, which are critical to shell building organisms. New observations from the eastern Bering Sea shelf show that remineralization of organic matter exported from surface waters rapidly increases bottom water CO<sub>2</sub> concentrations over the shelf in summer and fall, suppressing  $\Omega$  values. The removal of CO<sub>2</sub> from surface waters by high rates of phytoplankton primary production increases  $\Omega$  values between spring and summer, but these increases are partly counteracted by mixing with sea ice melt water and terrestrial river runoff that have low  $\Omega$  values. While these environmental processes play an important role in creating seasonally low saturation states, ocean uptake of anthropogenic CO<sub>2</sub> has shifted  $\Omega$  values for aragonite to below the saturation horizon in broad regions across the shelf for at least several months each year. Furthermore, we also report that calcite became undersaturated in September of 2009 in the bottom waters over the shelf. The reduction in CaCO<sub>3</sub> mineral saturation states could have profound implications for several keystone calcifying species in the Bering Sea, particularly the commercially important crab fisheries. **Citation:** Mathis, J. T., J. N. Cross, and N. R. Bates (2011), The role of ocean acidification in systemic carbonate mineral suppression in the Bering Sea, *Geophys. Res. Lett.*, **38**, L19602, doi:10.1029/2011GL048884.

## 1. Introduction

[2] It has been widely shown that the uptake of anthropogenic CO<sub>2</sub> by the oceans [Sabine *et al.*, 2004; Sabine and Feely, 2007] has a significant effect on marine biogeochemistry by reducing seawater pH [Feely *et al.*, 2009; Caldeira and Wickett, 2003] and the saturation states ( $\Omega$ ) of important calcium carbonate (CaCO<sub>3</sub>) minerals [Feely *et al.*, 2004; Orr *et al.*, 2005; Caldeira and Wickett, 2005] through a process termed ocean acidification. Seawater exhibiting undersaturated conditions (i.e.,  $\Omega < 1$ ) is potentially corrosive for biogenic CaCO<sub>3</sub> minerals such as aragonite, calcite

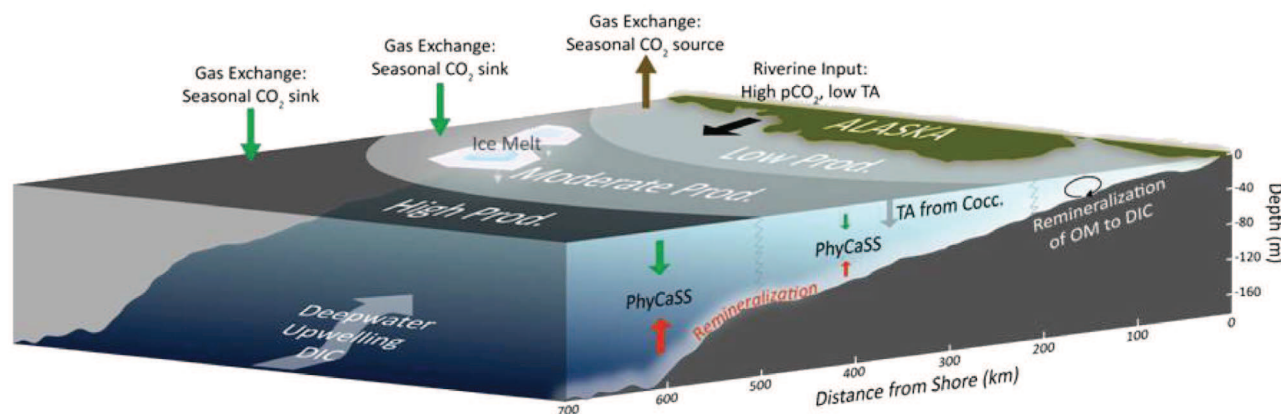
and high-Mg calcite. The reduction of CaCO<sub>3</sub> mineral saturation states in the surface ocean and along continental margins could have potentially negative consequences for benthic and pelagic calcifying organisms, and entire marine ecosystems [Fabry *et al.*, 2008; Feely *et al.*, 2010]. Of even greater concern is the rate at which ocean acidification and CaCO<sub>3</sub> mineral saturation state suppression are progressing, particularly in the high latitude regions of the North Pacific Ocean [Byrne *et al.*, 2010; Fabry *et al.*, 2009] where mixing processes and colder temperatures naturally precondition the water column to have lower pH and  $\Omega$  values compared to more temperate ocean environments.

[3] Recent observations in the sub-arctic North Pacific Ocean [Mathis *et al.*, 2011] have already revealed areas of seasonal CaCO<sub>3</sub> mineral  $\Omega$  suppression. Aragonite undersaturation has been observed throughout the water column, while models project widening areas of aragonite undersaturation in the region during the next several decades [Steinacher *et al.*, 2009]. This has potentially negative consequences for the region because the expansive continental shelf of the eastern Bering Sea sustains a commercially valuable fishery [Cooley and Doney, 2009; Cooley *et al.*, 2009] that produces approximately 47% of the US fish catch by weight. This marine ecosystem is critical to both the regional and national economy as well as subsistence communities in Alaska who rely heavily on the seasonal fish catch as their primary source of protein. These new findings show that the eastern Bering Sea will likely be one of the first ocean acidification impact zones for US national interests. Therefore, it is critical to gain a better understanding of both the natural and anthropogenic controls on CaCO<sub>3</sub> mineral suppression in the region.

[4] On the eastern Bering Sea shelf, a seasonal divergence in pH and  $\Omega$  is observed between surface and subsurface waters, driven primarily by the biology of the system. During the spring phytoplankton bloom, high rates of NCP effectively remove CO<sub>2</sub> from the surface waters creating a strong seasonal disequilibrium with the atmosphere [Bates *et al.*, 2011], but also increasing pH and  $\Omega$  values by ~0.1 and ~1 respectively [Mathis *et al.*, 2011]. The vertical export of organic matter and its subsequent seasonal remineralization at depth, induces a significant build-up of CO<sub>2</sub> in bottom waters (i.e.  $p\text{CO}_2$  increases) and concurrent suppression of CaCO<sub>3</sub> mineral  $\Omega$  values. The seasonal divergence of pH and  $\Omega$  in surface and subsurface waters has been described in terms of a "Phytoplankton-Carbonate Saturation State" (PhyCaSS) Interaction where significant interaction and feedback between ocean biology and seawater carbonate chemistry occurs. This process has been observed in the Chukchi Sea [Bates *et al.*, 2009; Bates and Mathis, 2009], and is likely a typical feature of highly productive polar and sub-polar shelves. In 2008, subsurface waters of the eastern Bering Sea

<sup>1</sup>School of Fisheries and Ocean Sciences, University of Alaska Fairbanks, Fairbanks, Alaska, USA.

<sup>2</sup>Bermuda Institute of Ocean Sciences, Ferry Reach, Bermuda, UK.



**Figure 1.** Generalized description of the processes affecting the carbonate chemistry of the eastern Bering Sea shelf. The influx of runoff from the coast delivers water with high  $p\text{CO}_2$ , low TA, and moderate concentrations of dissolved organic matter (OM). The high  $p\text{CO}_2$  of the water creates a seasonal source of  $\text{CO}_2$  to the atmosphere while reducing carbonate mineral saturation states. Offshore, the upper water column is dominated by sea ice melt in late spring and summer that creates a highly stratified surface layer where primary production is controlled by the confluence of coastal waters rich in micronutrients and basin water replete in macronutrients. Seasonally high rates of NCP lead to a rapid drawdown of  $\text{CO}_2$  at the surface creating a strong seasonal sink for atmospheric  $\text{CO}_2$ . In 2009, a coccolithophore (Cocc.) bloom was observed in the intermediate shelf waters and lowered TA concentrations at the surface. The varying degree of export production at the surface determined the amount of remineralization that occurred at depth which ultimately controlled saturation states. This PhyCaSS interaction can be observed to varying degrees across the shelf.

shelf became undersaturated with respect to aragonite (but not calcite) [Mathis *et al.*, 2011]. It has also been shown that the addition of anthropogenic  $\text{CO}_2$  to the ocean augments this natural seasonal interaction between ocean biology and seawater carbonate chemistry, tipping subsurface waters below the saturation state threshold ( $\Omega_{\text{aragonite}} = 1$ ) for aragonite [Mathis *et al.*, 2011]. In this paper, we show that subsurface waters of the eastern Bering Sea shelf in 2009 exhibits a greater degree of undersaturation than previous years, becoming nearly undersaturated with respect to calcite in addition to aragonite. We use these observations to illustrate how both natural and anthropogenic processes control  $\Omega$ , and how increasing levels of atmospheric  $\text{CO}_2$  could push the Bering Sea closer to a tipping point that could be detrimental for calcifying organisms.

## 2. Methods

[5] Seasonal dissolved inorganic carbon (DIC) and total alkalinity (TA) measurements were made along two east-west transects (see Figure S1 in the auxiliary material)<sup>1</sup> over the shelf during spring (April/May), summer (July), and fall (September) cruises in the eastern Bering Sea in 2009 as part of the Bering Ecosystem Study (BEST) project. Samples were collected with 10 m resolution from the surface to 50 m, with 25 m resolution from 50 m to 100 m, and with 50 m resolution from 100 m to 300 m. Conductivity-temperature-depth samples were collected by the NOAA Eco-Foci group on downcasts with a Seabird 911-plus system using dual temperature, conductivity, and oxygen sensors. Both salinity and Winkler oxygen calibrations were performed in post-processing. Nutrient samples for phosphate and silicate were also provided by the Eco-Foci group, with sample collection

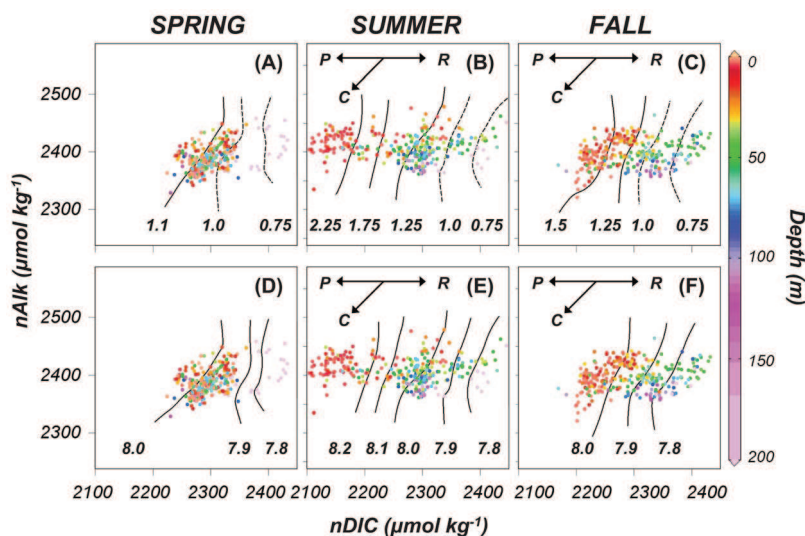
and analysis performed according to the protocols of Gordon *et al.* [1993].

[6] Seawater samples for DIC and TA were drawn from Niskin bottles into pre-cleaned  $\sim 300$  mL borosilicate bottles and poisoned with mercuric chloride ( $\text{HgCl}_2$ ) to halt biological activity. Samples were analyzed using a highly precise and accurate gas extraction/coulometric detection system [Bates, 2001]. The analytical system consists of a VINDTA 3C (Versatile Instrument for the Detection of Total Alkalinity) coupled to a  $\text{CO}_2$  coulometer. TA samples were determined by potentiometric titration using the VINDTA 3C. Routine analyses of Certified Reference Materials (CRMs, provided by A.G. Dickson, Scripps Institution of Oceanography) ensured that the accuracy of the DIC and TA measurements were within 0.08% ( $\sim 1.5 \mu\text{moles kg}^{-1}$ ) and stable over time. Seawater  $\text{CaCO}_3$  saturation states for calcite ( $\Omega_{\text{calcite}}$ ) and aragonite ( $\Omega_{\text{aragonite}}$ ) were calculated with CO2SYS version 1.05 from DIC, TA, temperature, salinity, phosphate, and silicate data using the thermodynamic model of Lewis and Wallace [1995], using the borate dissociation constant of Dickson [1990]; the silicate and phosphate dissociation constants of Dickson and Goyet [1994]; the carbonic acid dissociation constants of Mehrbach *et al.* [1973] as refit by Dickson and Millero [1987]; and the  $\text{CO}_2$  solubility equations of Weiss [1974]. Uncertainty in the calculation of  $\Omega_{\text{calcite}}$  and  $\Omega_{\text{aragonite}}$  were  $\sim 0.02$ .

[7] Sea ice cores were collected at seven locations across the Bering Sea shelf during the spring cruise. Cores were partitioned into 10 cm sections. Until analysis, these cores were kept frozen. For analysis, cores were allowed to thaw and meltwater was transferred into borosilicate bottles, poisoned with  $\text{HgCl}_2$  and analyzed for DIC and TA as above.

[8] Satellite True-color images were created from Modis Aqua Level 0 files which were downloaded from NASA's ocean color website (oceancolor.gsfc.nasa.gov). They were

<sup>1</sup>Auxiliary materials are available in the HTML. doi:10.1029/2011GL048884.



**Figure 2.** Scatter plots of (a–c) normalized total alkalinity (nAlk) and normalized DIC (nDIC) by depth (color) with aragonite saturation states ( $\Omega_{\text{arag}}$ ) and (d–f) pH contours in spring (Figures 2a and 2d), summer (Figures 2b and 2e) and fall (Figures 2c and 2f) of 2009. The dashed contour lines indicate undersaturation of aragonite minerals. Vectors indicate the relative influences of phytoplankton primary production ( $P$ ), remineralization ( $R$ ), and calcification ( $C$ ) on the dispersion of the data points. Between spring and summer, DIC drawdown in the surface layer and remineralization in subsurface waters greatly increased the dispersion along the x-axis. A wider range of  $\Omega_{\text{arag}}$  and pH observations indicated the influence of the PhyCaSS Interaction. Between spring and fall, increases in DIC from air-sea exchange and vertical diffusion decreased  $\Omega_{\text{arag}}$  and pH throughout the water column, and a higher frequency of bottom water undersaturations were observed relative to spring and summer. Also apparent in fall was the cumulative effects of the coccolithophore bloom, which decreased alkalinity values, particularly in surface waters.

processed using SeaDAS, a software package available through the same site.

### 3. Controls on Carbonate Mineral Saturation States

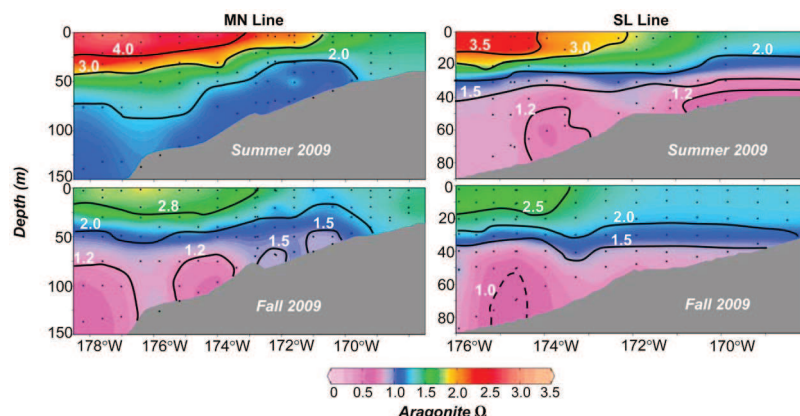
[9] The degree to which the  $\text{CaCO}_3$  mineral concentrations changed throughout 2009 at the surface and in the bottom waters of the eastern Bering Sea were related to several natural processes (Figure 1). In near-shore surface waters,  $\text{CaCO}_3$  mineral  $\Omega$  values are influenced by river runoff that has a high partial pressure of  $\text{CO}_2$  ( $p\text{CO}_2$ ) and low TA [Mathis et al., 2011; Striegl et al., 2007; Pan-Arctic River Transport of Nutrients, Organic Matter, and Suspended Sediments Project Arctic River biogeochemistry data set, 2010, unpublished raw data, <http://arcticgreatrivers.org/data.html#Datadownload>], which effectively suppresses  $\Omega$ . This effect is particularly pronounced in late spring and summer when discharge is at its peak. Over the middle and outer shelf, seasonal sea ice melt, which is low in carbonate ion concentrations due to brine rejection also acts to decrease  $\Omega$  values [Mathis et al., 2011]. Additionally, intermittent blooms of coccolithophores, which were observed during the summer of 2009 (Figures S1 and S2), also reduce TA, increase  $p\text{CO}_2$  and lower  $\Omega$  values. In contrast, the rapid and in some locations extensive drawdown of DIC within the mixed layer due to phytoplankton primary production compensates for most of the  $\text{CaCO}_3$  mineral suppression and increases pH between spring and summer, thus driving  $\Omega$  values higher near the surface [Mathis et al., 2011] (Figure 2). This is particularly true in the highly productive “green belt” (Figure S1) where large

particles are exported from surface to bottom waters, thereby rapidly transferring organic matter to depth.

[10] The remineralization of organic matter in the water column and sediment rapidly increased DIC concentrations in bottom waters between summer and fall of 2009, depressing  $\text{CaCO}_3$  mineral  $\Omega$  values. This process imparts a divergent trajectory for  $\Omega$  in bottom waters compared to the surface (Figure 2). Because of horizontal stratification, DIC from remineralization of organic matter accumulated in bottom waters, and subsequently depressed  $\text{CaCO}_3$  mineral  $\Omega$  values to a state of undersaturation (particularly for aragonite). These conditions were maintained until surface cooling, deep mixing events and the production of brine from ice formation that occurs late in the fall mix the water column and create more uniform concentrations of DIC and  $\Omega$ .

[11] TA was removed from the mixed layer in significant quantities in 2009 (Figure 2). Between spring and summer, TA concentrations along the SL line decreased nearly twice as much ( $\sim 100 \mu\text{moles kg}^{-1}$ ) as along the MN line ( $\sim 50 \mu\text{moles kg}^{-1}$ ). As in 2008, a large portion of this drawdown was due to dilution from ice melt and river runoff [Mathis et al., 2011], but given the much larger decreases in 2009 and the deeper penetrations of TA removal in the mixed layer, we estimate that coccolithophores were likely responsible for  $\sim 50\%$  of the decrease in TA. Accordingly, the highest drawdown of TA corresponded to SeaWiFS satellite images that showed the locations of the coccolithophore blooms (Figure S2). Lower concentrations (relative to spring values) of TA persisted into the fall since there were no immediate sources of alkalinity to the shelf due to carbonate-poor drainage basins in western Alaska [Brabets et al., 2000; Mathis et al., 2011]. The low alkalinity conditions were likely





**Figure 3.** Observations of aragonite (shown in color) and calcite (shown with black contour lines) saturation states ( $\Omega$ ) along the MN and SL transects lines in summer and fall of 2009. The dashed contour line indicates the location of waters undersaturated in calcite.

sustained until winter mixing brought bottom waters with higher TA concentrations to the surface.

[12] Observations along the SL line in spring showed that both aragonite and calcite were supersaturated in the water column with fairly uniform distributions ( $\Omega_{\text{aragonite}} \sim 1.5$  and  $\Omega_{\text{calcite}} \sim 2.5$ ) from the surface to the bottom. Over the outer shelf, the saturation states of both aragonite and calcite were lower, with aragonite being undersaturated at depths  $>60$  m. The lower saturation states near the shelf-break were likely due to the influence of deeper Bering Sea water with higher DIC concentrations [Mathis et al., 2011]. Along the MN line,  $\Omega$  values were again fairly uniform throughout the water column at  $\sim 1.5$  and  $\sim 2.5$ , respectively for  $\Omega_{\text{arg}}$  and  $\Omega_{\text{cal}}$  over the entire shelf.

[13] Between spring and summer, there were a number of important changes along both transects as the water column horizontally stratified and primary production dominated  $\Omega$  in the mixed layer [Cross et al., 2011]. Along the MN line in summer,  $\Omega_{\text{aragonite}}$  and  $\Omega_{\text{calcite}}$  values increased in offshore surface waters, particularly in the region of the “green belt” where DIC drawdown was highest. Beneath this layer though, high rates of export production and the remineralization of organic matter [Cross et al., 2011] suppressed  $\Omega$  causing aragonite to be at or below 1.0, while  $\Omega_{\text{calcite}} < 2.0$  (Figure 3) over nearly the entire shelf from  $\sim 50$  m to the bottom. Nearshore waters ( $\sim 0$ – $40$  m) had higher  $\Omega$ , likely due to limited phytoplankton primary production/export production in response to lower macronutrient concentrations.

[14] Between summer and fall,  $\Omega$  values in the surface waters along the MN line decreased (Figure 3) in response to  $\text{CO}_2$  uptake from the atmosphere and some remineralization, which increased DIC concentrations, returning  $\Omega$  values closer to pre-bloom levels. The suppression of  $\text{CaCO}_3$  mineral saturation continued below 50 m as remineralization contributed more DIC to the water column. Aragonite became highly undersaturated ( $<0.5$ ) over nearly the entire shelf and  $\Omega_{\text{calcite}} < 1.5$  near the bottom over the middle shelf and  $\Omega_{\text{calcite}} < 1.2$  over the outer shelf.

[15] The suppression of  $\text{CaCO}_3$   $\Omega$  values from spring to fall was even greater along the SL line (Figure 3). In summer, waters were at or below the saturation horizon for aragonite over the entire shelf below 40 m and calcite values

ranged from 1.1–1.5. This trend continued into fall when the lowest  $\Omega_{\text{arg}}$  ( $\sim 0.4$ ) were observed directly beneath green belt. The accumulation of DIC at this location was high enough to drive  $\Omega_{\text{calcite}}$  to less than 1.0 at water depths of 50–80 m. Calcite undersaturation was not observed in 2008, but as noted earlier, rates of NCP in the region of the green belt was higher in 2009 compared to 2008 which in turn, likely led to greater export and therefore greater remineralization over this part of the shelf.

[16] While our data clearly shows that  $\text{CaCO}_3$  mineral  $\Omega$  values were suppressed in the Bering Sea to levels that are potentially harmful to marine calcifiers, particularly in late summer and fall, some of this reduction is natural (i.e. related to the normal export of organic matter). Without an exact concentration of anthropogenic  $\text{CO}_2$  over the shelf, we cannot quantify the amount of suppression driven by the intrusion of anthropogenic  $\text{CO}_2$  with certainty. However, it is possible to make a conservative estimate because these shelf waters are derived from the North Pacific Ocean, where anthropogenic  $\text{CO}_2$  concentrations range between 40–50  $\mu\text{moles kg}^{-1}$ . We assumed that this water moved along isopycnals from the North Pacific Ocean feeding into the Bering Sea. In order to determine the impact that this additional  $\text{CO}_2$  had on  $\Omega$  in 2009 we subtracted it (45  $\mu\text{moles kg}^{-1}$  from all depths and at all locations) from our observed DIC values in spring, summer and fall while leaving all of the other parameters (TA, salinity, temperature, silicate and phosphate) constant, and recalculated  $\Omega$  using CO2SYS as described above. These results showed that without anthropogenic  $\text{CO}_2$  in the water column, calcite was supersaturated at all locations throughout the year and aragonite  $\Omega$  rose above 1 at all locations except near the bottom of the outer shelf in fall along the SL line. At the surface, when anthropogenic  $\text{CO}_2$  was removed,  $\Omega$  were higher in summer and remained so into the fall even as air-sea exchange of  $\text{CO}_2$  likely began to equilibrate the surface ocean with the atmosphere.

#### 4. Conclusions

[17] The eastern Bering Sea shelf is a critically important habitat for a number of keystone species, some of which are vital to the regional economy. Combined with previous

studies, our recent results from the area in spring, summer and fall of 2009 show that the saturation states of the two most important  $\text{CaCO}_3$  minerals are controlled by a number of natural processes that cumulatively create conditions in summer and fall that suppress  $\Omega$  in the water column, particularly below the surface mixed layer. As shown above, in 2009, these processes in conjunction with the cumulative absorption of atmospheric  $\text{CO}_2$  resulted in the appearance of shelf wide aragonite undersaturations and areas of calcite undersaturation. The continued uptake of atmospheric  $\text{CO}_2$  will likely push the Bering Sea seawater carbonate chemistry towards a tipping point that has negative implications for some calcifying organisms [Ries *et al.*, 2009].

[18] While seasonal freshwater from sea ice melt and river runoff suppress saturation states in surface waters, seasonally high rates of primary production raise pH and saturation states by removing  $\text{CO}_2$  [Mathis *et al.*, 2011]. In most cases, the removal of  $\text{CO}_2$  by phytoplankton primary producers is more than enough to compensate for  $\text{CaCO}_3$  mineral  $\Omega$  suppression causing a net increase in saturation states between spring and summer [Mathis *et al.*, 2011]. Saturation states begin to decrease to pre-bloom levels between summer and fall due to the uptake of  $\text{CO}_2$  via air-sea exchange [Mathis *et al.*, 2011; Bates *et al.*, 2011]. As average  $\text{CO}_2$  concentrations increase in the surface waters, saturation states will decrease and seasonal  $\text{CO}_2$  drawdown will not be able to fully compensate. In addition, warmer temperatures in the region will likely lead to a more active hydrological cycle [Huntington, 2006] bringing more river water that has low  $\text{CaCO}_3$  mineral  $\Omega$  values to the inner shelf, while seasonal sea ice melting will continue to suppress saturation states in the surface waters offshore. If the now infrequent coccolithophore blooms become a regular phenomenon in the eastern Bering Sea shelf they will add yet another removal mechanism for TA in the surface waters, which will lead to enhanced  $\text{CaCO}_3$  mineral suppression in the long term.

[19] The bottom waters of the Bering Sea are even closer to a possible threshold for  $\text{CaCO}_3$  mineral undersaturation. For at least several months (July–September) there are expansive areas over the shelf where waters become undersaturated with respect to aragonite and there is new evidence to show calcite undersaturation was also present in 2009 in a few localized areas, which are co-located with the highest rates of export production. As anthropogenic  $\text{CO}_2$  inventories continue to increase in these waters, the saturation states will be further suppressed going forward in time. Each year, the remineralization of export production will further suppress saturation states along the bottom and undersaturated conditions will persist longer. If primary production and/or export production increases in the Bering Sea shelf in response to warming or changes in species composition, it could accelerate the pace of change in carbonate mineral concentrations near the bottom.

[20] Finally, we hypothesize that when surface water saturation states are reduced and the bottom waters are persistently undersaturated, deep winter mixing [Coachman, 1986; Stabenro *et al.*, 2006] will cause the entire water column to drop below the saturation horizon, leaving the springtime water column under the ice undersaturated in aragonite. For a time, phytoplankton primary production will alleviate the undersaturations creating periods of higher  $\text{CaCO}_3$  mineral concentrations, but eventually even these

periods will be diminished and the Bering Sea will be persistently undersaturated with respect to aragonite likely by mid-century, with broad regions of seasonal calcite undersaturation following later.

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- N. R. Bates, Bermuda Institute of Ocean Sciences, 17 Biological Station Ln., Ferry Reach, Bermuda, GE01, UK.
- J. N. Cross and J. T. Mathis, School of Fisheries and Ocean Sciences, University of Alaska Fairbanks, 245 O'Neill Bldg., Fairbanks, AK 99775, USA. (jmathis@sfos.uaf.edu)