

## Evidence for Upwelling of Corrosive “Acidified” Water onto the Continental Shelf

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**The absorption of atmospheric carbon dioxide into the ocean lowers the pH of the waters. This so-called ocean acidification could have important consequences for marine ecosystems. In order to better understand the extent of this ocean acidification in coastal waters, we conducted hydrographic surveys from central Canada to northern Mexico. We observed seawater that is undersaturated with respect to aragonite upwelling onto large portions of the continental shelf, reaching depths of approximately 40-120 m along most transect lines and all the way to the surface on one transect off northern California. While seasonal upwelling of the undersaturated waters onto the shelf is a natural phenomenon in this region, the ocean uptake of anthropogenic CO<sub>2</sub> has increased the areal extent of the affected area.**

Over the past 250 years the release of carbon dioxide (CO<sub>2</sub>) from industrial and agricultural activities has resulted in atmospheric CO<sub>2</sub> concentrations that have increased by about 100 parts per million (ppm). The atmospheric concentration of CO<sub>2</sub> is now higher than it has been for at least the last 650,000 years, and is expected to continue to rise at an increasing rate, leading to significant changes in our climate by the end of this century (1). Since the beginning of the industrial era, the oceans have absorbed approximately 127 ± 18 billion metric tons of carbon as carbon dioxide from the atmosphere, or about one third of the anthropogenic carbon emissions released (2). This process of absorption of anthropogenic CO<sub>2</sub> has benefited humankind by significantly reducing the greenhouse gas levels in the atmosphere and minimizing some of the impacts of global warming. However, the ocean’s daily uptake of 30 million metric tons of carbon dioxide is significantly impacting its chemistry and biology. Recent hydrographic surveys and modeling studies have confirmed that the uptake of anthropogenic CO<sub>2</sub> by the oceans has resulted in a lowering of seawater pH by about 0.1 since the beginning of the industrial revolution (3–7). This

phenomenon, which is commonly called “ocean acidification,” could affect some of the most fundamental biological and geochemical processes of the sea in the coming decades and could seriously alter the fundamental structure of pelagic and benthic ecosystems (8).

Estimates of future atmospheric and oceanic carbon dioxide concentrations, based on the Intergovernmental Panel on Climate Change (IPCC) CO<sub>2</sub> emission scenarios and general circulation models, indicate that atmospheric carbon dioxide levels could exceed 500 parts per million (ppm) by the middle of this century, and 800 ppm near the end of the century. This increase would result in a surface water pH decrease of approximately 0.4 pH units, and a corresponding 50% decrease in carbonate ion concentration by the end of the century (5, 9). Such rapid changes are likely to negatively impact marine ecosystems, seriously jeopardizing the multi-faceted economies that currently depend on them (10).

The reaction of CO<sub>2</sub> with seawater reduces the availability of carbonate ions that are necessary for calcium carbonate (CaCO<sub>3</sub>) skeleton and shell formation for a number of marine organisms such as corals, marine plankton, and shellfish. The extent to which the organisms are affected is largely dependent upon the calcium carbonate (CaCO<sub>3</sub>) saturation state (Ω), which is the product of the concentrations of Ca<sup>2+</sup> and CO<sub>3</sub><sup>2-</sup> divided by the apparent stoichiometric solubility product for either aragonite or calcite:

$$\Omega_{\text{arag}} = [\text{Ca}^{+2}] [\text{CO}_3^{-2}] / K' \text{sp}_{\text{arag}} \quad (1)$$

$$\Omega_{\text{cal}} = [\text{Ca}^{+2}] [\text{CO}_3^{-2}] / K' \text{sp}_{\text{cal}} \quad (2)$$

where the calcium concentration is estimated from the salinity, and the carbonate ion concentration is calculated from the dissolved inorganic carbon (DIC) and total alkalinity (TA) measurements (11). In regions where Ω<sub>arag</sub> or Ω<sub>cal</sub> is > 1.0 the formation of shells and skeletons is favored. Below a value of 1.0 the water is corrosive and dissolution of pure aragonite and unprotected aragonite shells will begin to occur (12). Recent studies have demonstrated that in many regions of the ocean the aragonite saturation horizon shoaled as much

as 40–200 m as a direct consequence of the uptake of anthropogenic CO<sub>2</sub> (3, 5, 6). It is shallowest in the northeastern Pacific Ocean, only 100–300 m from the ocean surface, allowing for the transport of undersaturated waters onto the continental shelf during periods of upwelling.

In May and June of 2007, we conducted a North American Carbon Program (NACP) West Coast Cruise on the Research Ship *Wecoma* along the continental shelf of western North America, completing a series of 13 cross-shelf transects from Queen Charlotte Sound, Canada to San Gregorio Baja California Sur, Mexico (Fig. 1). Full water column conductivity-temperature-depth-rosette (CTDR) stations were occupied at specified locations along each transect (Fig. 1). Water samples were collected in modified Niskin-type bottles and analyzed for DIC, TA, oxygen, nutrients and dissolved and particulate organic carbon. Aragonite and calcite saturation, pH<sub>sw</sub>, and pCO<sub>2</sub> were calculated from the DIC and TA data (11).

The central and southern coastal region off western North America is strongly influenced by seasonal upwelling which typically begins in early spring when the Aleutian low pressure system moves to the northwest and the Pacific High moves northward, resulting in a strengthening of the northwesterly winds (13, 14). These winds drive net surface water Ekman transport offshore, which induces the upwelling of CO<sub>2</sub>-rich intermediate depth (100–200 m) offshore waters onto the continental shelf. The upwelling lasts until late summer or fall when winter storms return.

During the cruise, various stages and strengths of upwelling were observed from line 2 off central Vancouver Island to line 11 off Baja California, Mexico. We observed recent upwelling on lines 5 and 6 near the Oregon-California border. Coincident with the upwelled waters, we found evidence for undersaturated, low pH seawater in the bottom waters as depicted by  $\Omega_{\text{arag}}$  values < 1.0 and pH values < 7.75. The corrosive waters reached mid-shelf depths of approximately 40–120 m along lines 2–4, and 7–13 (Fig. 1). In the region of the strongest upwelling (line 5), the isolines of  $\Omega_{\text{arag}} = 1.0$ , DIC = 2190 and pH = 7.75 closely followed the 26.2 potential density surface (Fig. 2). This density surface shoaled from a depth of ~150 m in the offshore waters and breached the surface over the shelf near the 100 m bottom contour, approximately 40 km from the coast. This shoaling of the density surfaces and CO<sub>2</sub>-rich waters as one approaches land is typical of strong coastal upwelling conditions (15–18). The surface water pCO<sub>2</sub> on the 26.2 potential density surface was about 850  $\mu\text{atm}$  near the shelfbreak and higher inshore (Fig. 2), possibly enhanced by respiration processes on the shelf (17). These results indicate that the upwelling process caused the entire water column shoreward of the 50 m bottom contour to become undersaturated with respect to aragonite, a condition that was not predicted to occur in open-ocean

surface waters until 2050 (5). On line 6, the next transect south, the undersaturated water was close to the surface at approximately 22 km from the coast. The lowest  $\Omega_{\text{arag}}$  values (<0.60) observed in the near-bottom waters of the continental shelf corresponded with pH values close to 7.5. Since the calcite saturation horizon is located between 225–400 m in this part of the northeastern Pacific (19), it is still too deep to shoal onto the continental shelf. Nevertheless, the calcite saturations values drop in the core of the upwelled water ( $\Omega_{\text{cal}} < 1.3$ ).

As noted, the North Pacific aragonite saturation horizons are among the shallowest in the global ocean (3). The uptake of anthropogenic CO<sub>2</sub> has caused these horizons to shoal by 50–100 m since pre-industrial times so that they are within the density layers that are currently being upwelled along the west coast of North America. Although much of the corrosive character of these waters is the natural result of respiration processes at intermediate depths below the euphotic zone, this region continues to accumulate more anthropogenic CO<sub>2</sub> and, therefore, the upwelling processes will expose coastal organisms living in the water column or at the seafloor to less saturated waters exacerbating the biological impacts of ocean acidification.

Based on our observed O<sub>2</sub> values and estimated O<sub>2</sub> consumption rates on the same density surfaces (20), the upwelled water off northern California (line 5) was last at the surface about 50 years ago when atmospheric CO<sub>2</sub> was about 65 ppm lower than today. The open ocean anthropogenic CO<sub>2</sub> distributions in the Pacific have been estimated previously (19, 4, 21). By determining the density-dependence of anthropogenic CO<sub>2</sub> distributions in the eastern-most North Pacific stations of the Sabine et al (21) data set, we estimate that these upwelled waters contain approximately  $31 \pm 4$   $\mu\text{mol kg}^{-1}$  anthropogenic CO<sub>2</sub> (fig. S2). Removing this signal from the DIC increases the aragonite saturation state of the waters by about 0.2 units. Thus, without the anthropogenic signal, the equilibrium aragonite saturation level ( $\Omega_{\text{arag}} = 1$ ) would be deeper by about 50 m across the shelf, and no undersaturated waters would reach the surface. Water already in transit to upwelling centers is carrying increasing anthropogenic CO<sub>2</sub> and more corrosive conditions to the coastal oceans of the future. Thus the undersaturated waters, which were mostly a problem for benthic communities in the deeper waters near the shelf break in the pre-industrial era, have shoaled closer to the surface and near the coast because of the additional inputs of anthropogenic CO<sub>2</sub>.

These observations clearly show that seasonal upwelling processes enhance the advancement of the corrosive deep water into broad regions of the North American western continental shelf. Since the region experiences seasonal periods of enhanced aragonite undersaturation, it is important to understand how the indigenous organisms deal with this

exposure and whether or not future increases in the range and intensity of the corrosiveness will affect their survivorship. Presently, little is known about how this intermittent exposure to corrosive water might impact the development of larval, juvenile and adult stages of aragonitic calcifying organisms or finfish that populate the neritic and benthic environments in this region and fuel a thriving economy. Laboratory and mesocosm experiments show that these changes in saturation state may cause significant changes in overall calcification rates for many species of marine calcifiers including corals, coccolithophores, foraminifera and pteropods, which are a significant food source for local juvenile salmon (8, 22–30). Similar decreases in calcification rates would be expected for edible mussels, clams and oysters (22, 31). Other research indicates that many species of juvenile fish and shellfish of significant economic importance to coastal regions are highly sensitive to higher-than-normal CO<sub>2</sub> levels such that high rates of mortality are directly correlated with the higher CO<sub>2</sub> levels (31, 32). While comprehensive field studies of organisms and their response to sporadic increases in CO<sub>2</sub> along the western North American coast are lacking, current studies suggest that further research under field conditions is warranted. Our results show for the first time that a large section of the North American continental shelf is impacted by ocean acidification. Other continental shelf regions may also be impacted where anthropogenic CO<sub>2</sub>-enriched water is being upwelled onto the shelf.

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## Supporting Online Material

[www.sciencemag.org/cgi/content/full/1155676/DC1](http://www.sciencemag.org/cgi/content/full/1155676/DC1)  
Materials and Methods  
Figs. S1 and S2

## References

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**Fig. 1.** Distribution of the depths of the undersaturated water (aragonite saturation  $< 1.0$ ;  $\text{pH} < 7.75$ ) on the continental shelf of western North America from Queen Charlotte Sound, Canada to San Gregorio Baja California Sur, Mexico. On transect lines 5 the corrosive water reaches all the way to the surface in the inshore waters near the coast. The black dots represent station locations.

**Fig. 2.** Vertical sections of: (A) temperature, (B) aragonite saturation, (C) pH, (D) DIC and (E)  $p\text{CO}_2$ , on transect line 5 off Pt. St. George, California. Note that the potential density surfaces are superimposed on the temperature section. The 26.2 potential density surface delineates the location of the first instance of the undersaturated water being upwelled from depths of 150-200 m onto the shelf and outcropping at the surface near the coast. The black dots represent sample locations.



