

Ocean acidification of the North Pacific Ocean

by Richard A. Feely, Victoria J. Fabry and John M. Guinotte

Abstract

The addition of fossil fuel carbon dioxide to the atmosphere is rapidly changing seawater chemistry and the calcium carbonate saturation state of the world's oceans as a result of the acidifying effects of CO₂ on seawater. This acidification makes it more difficult for many marine organisms (*e.g.*, corals, plankton, calcareous algae, and mollusks) to build skeletons, tests, and shells of calcium carbonate. Impacts on these calcifying organisms could lead to substantial changes in marine ecosystems. Repeat hydrographic and time-series data for the North Pacific show direct evidence for ocean acidification. These dramatic changes can be attributed, in most part, to anthropogenic CO₂ uptake by the ocean over the past several decades.

Introduction

Over the past two centuries the release of carbon dioxide (CO₂) from humankind's collective industrial and agricultural activities has resulted in atmospheric CO₂ concentrations that have risen from pre-industrial levels of about 280 ppmv (parts per million) to nearly 383 ppmv (Solomon *et al.*, 2007). The atmospheric concentration of CO₂ is now higher than experienced on Earth for at least the last 800,000 years, and is expected to continue to rise, leading to significant temperature increases in the atmosphere and oceans by the end of this century. The rate of current and projected increases in atmospheric CO₂ is

more than 100 times faster than has occurred over the last 650,000 years (Raven *et al.*, 2005; Kleypas *et al.*, 2006; Hoegh-Guldberg *et al.*, 2007). To date, the oceans have absorbed approximately 525 billion tons of carbon dioxide from the atmosphere, or about one third of the anthropogenic carbon emissions released during this period (Sabine and Feely, 2007). This natural process of absorption has benefited humankind by significantly reducing greenhouse gas levels in the atmosphere, thus minimizing some impacts of global warming. However, the ocean's daily uptake of 22 million tons of carbon dioxide is beginning to have a significant impact on the chemistry and biology of the oceans. For more than 25 years, an international group of PICES scientists has been conducting repeat hydrographic and chemical surveys of the North Pacific Ocean, documenting its response to increasing amounts of carbon dioxide being emitted to the atmosphere by human activities. These surveys, as well as the time-series data from Ocean Stations Aloha and Papa, have confirmed that the oceans are absorbing increasing amounts of carbon dioxide (**Fig. 1**). Both the hydrographic surveys and time-series data reveal that the chemical changes in seawater resulting from the absorption of carbon dioxide are lowering seawater pH (Caldeira and Wickett, 2003; 2005; Feely *et al.*, 2004; in press; Orr *et al.*, 2005; Solomon *et al.*, 2007). For example, the time-series data at Ocean Station Aloha shows an average pH decrease of approximately 0.02 units per decade in the Northeast Pacific (**Fig. 1**). It is now well established that the pH of our ocean surface waters has already fallen by about

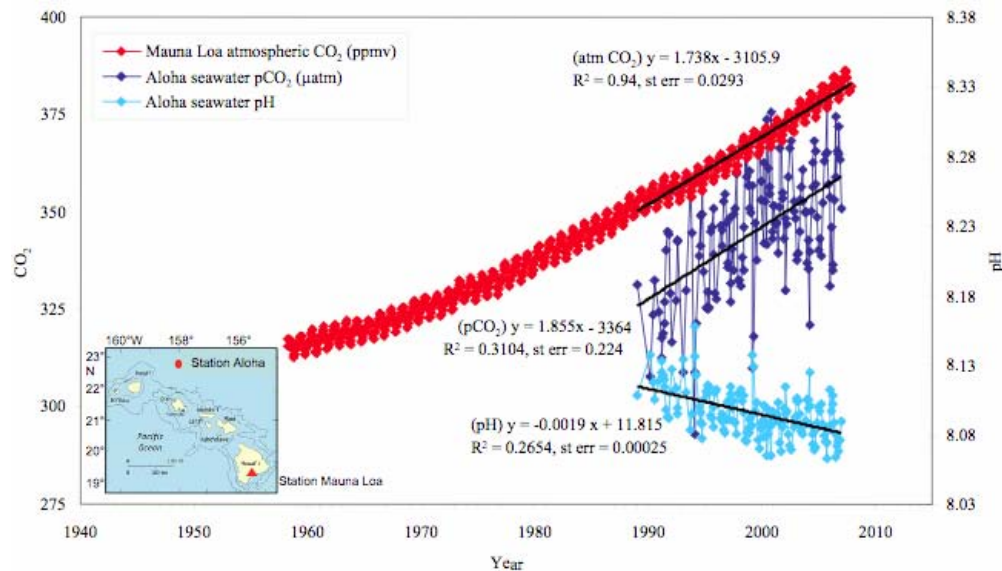
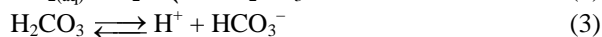
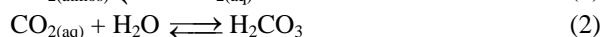


Fig. 1 Time series of atmospheric CO₂ at Mauna Loa (ppmv) and surface ocean pH and pCO₂ (µatm) at Ocean Station Aloha in the subtropical North Pacific Ocean. Note that the increase in oceanic CO₂ over the last 17 years is consistent with the atmospheric increase within the statistical limits of the measurements. Mauna Loa data: Dr. Pieter Tans, NOAA/ESRL (<http://www.esrl.noaa.gov/gmd/ccgg/trends/>); HOTS/Aloha data: Dr. David Karl, University of Hawaii (<http://hahana.soest.hawaii.edu>).

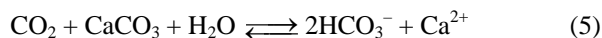
0.1 units from an average of about 8.21 to 8.10 since the beginning of the industrial revolution. Estimates of future atmospheric and oceanic carbon dioxide concentrations, based on the Intergovernmental Panel on Climate Change (IPCC) CO₂ emission scenarios and general circulation models, indicate that by the middle of this century, atmospheric carbon dioxide levels could reach more than 500 ppmv, and near the end of the century, they could be over 800 ppmv. This would result in a further surface water pH decrease of 0.2–0.3 pH, and the carbonate ion concentration would decrease almost 50 percent by the end of the century (Orr *et al.*, 2005). To put this in historical perspective, this surface ocean pH decrease would result in a pH that is lower than it has been for more than 20 million years (Feely *et al.*, 2004).

When carbon dioxide exchanges across the air–sea interface, the concentrations of carbon species in seawater are changed *via* a series of chemical reactions:



where the air–sea CO₂ exchange reaction (1) leads to an initial increase in dissolved CO₂. This dissolved CO₂ reacts with H₂O to form carbonic acid (2). Some of the carbonic acid quickly dissociates into a hydrogen ion and a bicarbonate ion (3). A fraction of the bicarbonate ions can then dissociate further into a hydrogen ion and a carbonate ion (4). These reactions are rapid and reversible, and the basic thermodynamics of these reactions in seawater are well known (Millero *et al.*, 2002) such that, at a pH of ~8.1, approximately 90% of the carbon is in the form of bicarbonate ion, 9% in the form of carbonate ion, and only about 1% of the carbon is in the form of dissolved CO₂.

The ocean’s ability to absorb more CO₂ from the atmosphere also depends on the extent of interactions of marine carbonates with CO₂ *via* the dissolution reaction:



The primary contributors to this reaction are the carbonate shells that are produced in the euphotic zone. Upon death, the carbonate shells fall through the water column and are either dissolved or deposited in shallow or deep-sea sediments. As the oceans become enriched in anthropogenic CO₂, the locations and extent of dissolution will increase as a function of the decrease in the CaCO₃ saturation state. The *in situ* degree of saturation of seawater with respect to calcite and aragonite is the ion product of the concentrations of calcium and carbonate ions, at the *in situ* temperature, salinity, and pressure, divided by the apparent stoichiometric solubility product (K_{sp}^*) for those conditions:

$$\Omega_{\text{arg}} = [\text{Ca}^{2+}] [\text{CO}_3^{2-}] / K_{sp, \text{arg}}^* \quad (6)$$

$$\Omega_{\text{cal}} = [\text{Ca}^{2+}] [\text{CO}_3^{2-}] / K_{sp, \text{cal}}^* \quad (7)$$

in which 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) data. Since the calcium to salinity ratio in seawater does not vary by more than a few percent, variations in the ratio of [CO₃²⁻] to the stoichiometric solubility product govern the degree of saturation of seawater with respect to aragonite and calcite. The interaction between CO₂ and seawater reduces the availability of carbonate ions which play an important role in shell formation for a number of CaCO₃ shell-forming organisms, including marine plankton, shellfish and cold-water corals. This phenomenon of decreasing pH and carbonate ion concentration, which is called “ocean acidification”, could affect the oceans’ most fundamental biological and geochemical processes in the coming decades. This rapidly emerging scientific issue has created serious concern across the scientific and fisheries resource management communities.

Saturation state changes in the North Pacific Ocean

Shell and skeleton formation is favored in regions of the North Pacific where the calcium carbonate saturation state is >1.0. Saturation state <1.0 indicates that waters are corrosive to CaCO₃, and dissolution will occur if the shells and skeletons are not protected. Saturation states are generally highest in the tropics and lowest in the high latitude regions because the solubility of CaCO₃ increases with decreasing temperature and increasing pressure. Therefore, there is significant shoaling of aragonite saturation horizons in the North Pacific north of 40°N, near the equator, and especially near the eastern boundary of the basin. High DIC levels occur in this region because enhanced upwelling brings deeper waters rich in DIC and nutrients to the upper ocean. In the waters off the Alaskan coast (north of 50°N) the aragonite saturation depth shoals to depths ranging from 90–150 m (Fig. 2).

Feely *et al.* (in press) provide maps of projected aragonite saturation states for the surface oceans for years 1765,

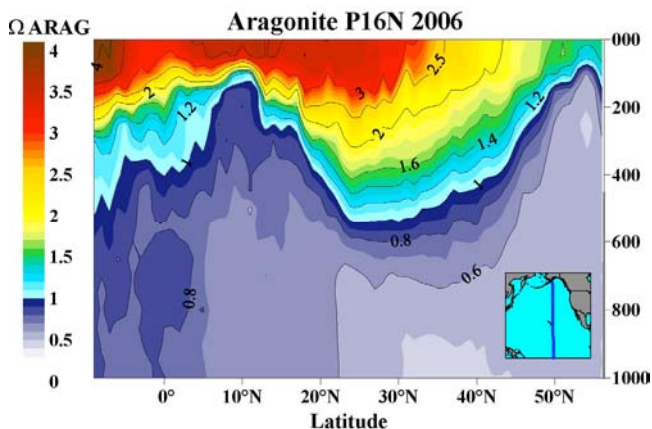


Fig. 2 Distribution of aragonite saturation along the March 2006 P16N transect along 152°W in the North Pacific (after Fabry *et al.*, in press).

1995, 2040 and 2100, which are based on the modeling work of Orr *et al.* (2005). The model results show that by the time atmospheric CO₂ reaches 780 ppmv, near the end of this century, the entire water column (from the ocean floor to the surface) will become undersaturated with respect to aragonite in some regions of the subarctic North Pacific. At this point, the average surface ocean carbonate ion concentration will have decreased by nearly 50%. The warm waters of the tropics and subtropics will remain supersaturated with respect to aragonite and calcite over the range of IPCC-projected atmospheric CO₂ concentrations. However, some upwelling areas in the low latitude regions are experiencing low aragonite saturation state conditions, and these waters are within depth ranges of several critically important pelagic species (Feely *et al.*, 2004). Priority areas for ocean acidification research are high latitude regions that are projected to experience the highest relative changes in carbonate chemistry within the century. Given the importance of coastal areas to fisheries and other marine resources and services, coastal ecosystems constitute another important target region where research is critically needed.

Effects of ocean acidification on marine ecosystems

Ongoing research suggests that elevated CO₂ levels may have deleterious impacts on commercially important fish. Silver seabream larvae exhibit very high mortality rates in CO₂-enriched waters (Ishimatsu *et al.*, 2004). Some experiments indicate that additional physiological stresses are also observed (Kleypas *et al.*, 2006; Fabry *et al.*, in press). Exposure of fish to lower pH levels can cause decreased respiration rates, changes in blood chemistry, and changes in enzymatic activity. The calcification rates of the edible mussel (*Mytilus edulis*) and Pacific oyster (*Crassostrea gigas*) decline linearly with increasing CO₂ levels (Gazeau *et al.*, 2007). Squid are especially sensitive to ocean acidification because it directly impacts their blood oxygen transport and respiration (Pörtner *et al.*, 2005). Sea urchins raised in lower-pH waters show evidence for inhibited growth due to their inability to maintain internal acid-base balance (Kurihara and Shirayama, 2004). Scientists have also seen a reduced ability of marine algae and animals to produce protective carbonate shells (Gattuso *et al.*, 1998; Langdon *et al.*, 2000; Riebesell *et al.*, 2000; Feely *et al.*, 2004; Orr *et al.*, 2005; Fabry *et al.*, in press). These organisms are important food sources for many marine species. One such example is a pteropod, a free-swimming mollusc that is eaten by organisms ranging in size from tiny zooplankton to whales. In particular, pteropods are an important food source for North Pacific juvenile salmon. Mackerel, pollock, herring and cod are also known to feed on pteropods. Many species of other marine calcifiers, such as coccolithophores (microscopic algae), foraminifera (microscopic protozoans), coralline algae (benthic algae), echinoderms (sea urchins and starfish), and mollusks (snails, clams, and squid) also exhibit a general decline in

their ability to produce shells with decreasing pH (Kleypas *et al.*, 2006; Fabry *et al.*, in press).

Since ocean acidification research is still in its infancy, it is impossible to predict exactly how individual species responses will transfer through marine food webs and impact the overall structure of marine ecosystems. It is clear, however, from the existing data and from the geologic record that some coral and shellfish species will be reduced in a high-CO₂ ocean. The rapid disappearance of many calcifying species in past extinction events has been attributed, in large part, to ocean acidification events (Zachos *et al.*, 2005). Over the next century, if CO₂ emissions are allowed to increase as predicted by the IPCC CO₂ emissions scenarios, humans may be responsible for increasing oceanic CO₂ to levels that are more corrosive to calcifying organisms than anytime since the last major extinction, over 65 million years ago. Thus, the decisions we make about our use of fossil-fuels for energy over the next several decades will have a profound influence on the future composition of marine ecosystems for centuries to millennia.

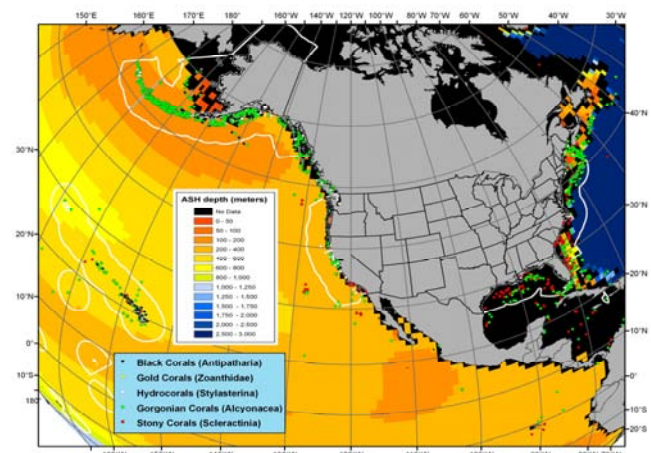


Fig. 3 Distribution of selected cold-water corals in U.S. coastal waters and the depth of aragonite saturation horizon for year 1995 (CO₂ = 365 ppmv). Note: very little model results exist for the coastal zone where the majority of cold water corals and commercial fisheries are located. Aragonite saturation data from Orr *et al.* (2005; modified from Guinotte *et al.*, 2006 and Morgan *et al.*, 2007).

The impact of ocean acidification on fisheries and coral reef ecosystems could significantly impact the U.S. and global economies. The U.S. is the third largest seafood consumer in the world, with total consumer spending for fish and shellfish around \$60 billion per year. Coastal and offshore commercial fishing generates upwards of \$30 billion per year and employs approximately 70,000 people. Nearly half of the U.S. fish catch is taken from the coastal waters surrounding Alaska. Increased ocean acidification may directly and/or indirectly influence fish populations because of large-scale changes in local ecosystem dynamics. It may also have detrimental impacts on the newly discovered cold-water corals in the Alaskan Aleutian Island region (Fig. 3, Guinotte *et al.*, 2006). The Aleutian

Islands have the highest abundance and diversity of cold-water corals found to date and 85% of commercially important fish species observed on submersible transects in this region were associated with corals (Heifetz *et al.*, 2005; Stone, 2006; Guinotte and Fabry, in press). Direct and/or indirect effects of ocean acidification on the cold-water coral ecosystems of the North Pacific will probably have significant impacts on associated species that depend on these organisms for food and shelter, including commercially important species (Guinotte and Fabry, in press).

Conclusions

Ocean acidification may be one of the most significant and far-reaching consequences of the buildup of anthropogenic carbon dioxide in the atmosphere. Results from laboratory, field and modeling studies, as well as evidence from the geological record, clearly indicate that marine ecosystems are highly susceptible to increases in oceanic CO₂ and corresponding decreases in pH. Corals and many other calcifying organisms will be increasingly affected by a decreased capability to produce their shells and skeletons. Other species of fish and shellfish will also be negatively impacted in their physiological responses due to a decrease in pH levels of their cellular fluids. Because of the very

clear potential for ocean-wide impacts of ocean acidification at all levels of the marine ecosystem, from the tiniest phytoplankton to zooplankton to fish and shellfish, we can expect to see significant impacts that are of immense importance to humankind. Ocean acidification is an emerging scientific issue, and much research is needed before the ecosystem responses are well understood. Even though ecosystem responses are not well known, the potential risk for negative environmental, economic and societal impacts is high and warrants serious and immediate attention. For these reasons, the national and international scientific communities have recommended a coordinated scientific research program with four major themes: (1) carbon system monitoring coupled with high-quality measurements tracking the vertical and latitudinal distributions and abundances of calcifying organisms; (2) calcification and physiological response studies under laboratory and field conditions; (3) environmental and ecosystem modeling studies; and (4) socio-economic risk assessments. This research will provide resource managers with the basic information they need to develop strategies for protection of critical species, habitats and ecosystems.

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Dr. Richard A. Feely's (Richard.A.Feely@noaa.gov) major research areas are carbon cycling in the oceans and ocean acidification processes. He received a B.A. in Chemistry from the University of St. Thomas, in St. Paul, Minnesota, in 1969. He then went to the Texas A&M University, where he received an M.S. degree in 1971 and a Ph.D. degree in 1974. Both of his post-graduate degrees were in Chemical Oceanography. He is a member of the Science Steering Committees for the U.S. Carbon Cycle Science Program, the U.S. Ocean Carbon and Climate Change Program, and the U.S. Ocean Carbon and Biochemistry Program. Dr. Feely has authored more than 160 refereed research publications. In PICES, he co-chaired WG 13 on CO₂ in the North Pacific, was a member of WG 17 on Biogeochemical data integration and synthesis, and now serves as a member of the Section on Carbon and climate.

Dr. Victoria J. Fabry (fabry@csusm.edu), Professor of Biological Sciences at California State University San Marcos, is a Biological Oceanographer whose research interests encompass the role of marine organisms in geochemical cycles. The response of calcifying organisms to ocean acidification and the dissolution kinetics of biogenic calcium carbonate in the upper ocean are two areas of her current work. She earned a Ph.D. in Biology at the University of California Santa Barbara, conducted post-doctoral work in marine chemistry at the Woods Hole Oceanographic Institution, and worked as a biogeochemist at the International Atomic Energy Agency's Marine Environmental Laboratory in Monaco. She is a member of numerous national and international committees concerned with ocean acidification research.

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Ocean acidification will be discussed in further detail at two PICES-supported international symposia.

International Symposium on the Effects of Climate Change on the World's Oceans

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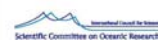
SCIENTIFIC PROGRAM	DEADLINES
Plenary and Invited Speakers Past and future variability and change in ocean climate - Theme 1.1: Observed climate changes - Theme 1.2: Climate model projections Interactions between climate variability and change and biogeochemical cycles - Theme 2.1: Marine carbon cycling and other biogeochemical cycles Theme 2.2: Ocean acidification and coral reef bleaching Impacts of climate variability and change on the coastal environment - Theme 3.1: Natural hazards, sea level rise and coastal erosion - Theme 3.2: Estuarine and wetland ecosystem functioning Impacts of climate change on marine ecosystems: Present status of our understanding - Theme 4.1: Impacts on lower trophic levels - Theme 4.2: Impacts on higher trophic levels Scenarios-mitigation-adaptation of impact of future climate change on the marine environment: from regional to global scale - Theme 5.1: Scenarios for polar, mid-latitude, sub-tropical, and tropical environments and ecosystems - Theme 5.2: Adaptation and mitigation of effects in the marine environment and ecosystems In addition to the Plenary and Theme Sessions, several workshops will be convened in conjunction with the symposium	Abstracts: January 15, 2008 Financial support: January 15, 2008 Registration reduced fee: February 15, 2008 Symposium Convenors: Luis Valdés - ICES William Peterson - PICES John Church - IOC Scientific Steering Committee: Richard Feely (U.S.A.) Michael Foreman (Canada) Roger Harris (U.K.) Ove Hoegh-Guldberg (Australia) Harald Loeng (Norway) Liana McManus (U.S.A./Philippines) Jorge Sarmiento (U.S.A.) Martin Visbeck (Germany) Akihiko Yatsu (Japan) Local Organizer: Instituto Espanol de Oceanografía (IEO) Centro Oceanografico de Gijón Symposium Secretariat: PICES - Canada

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