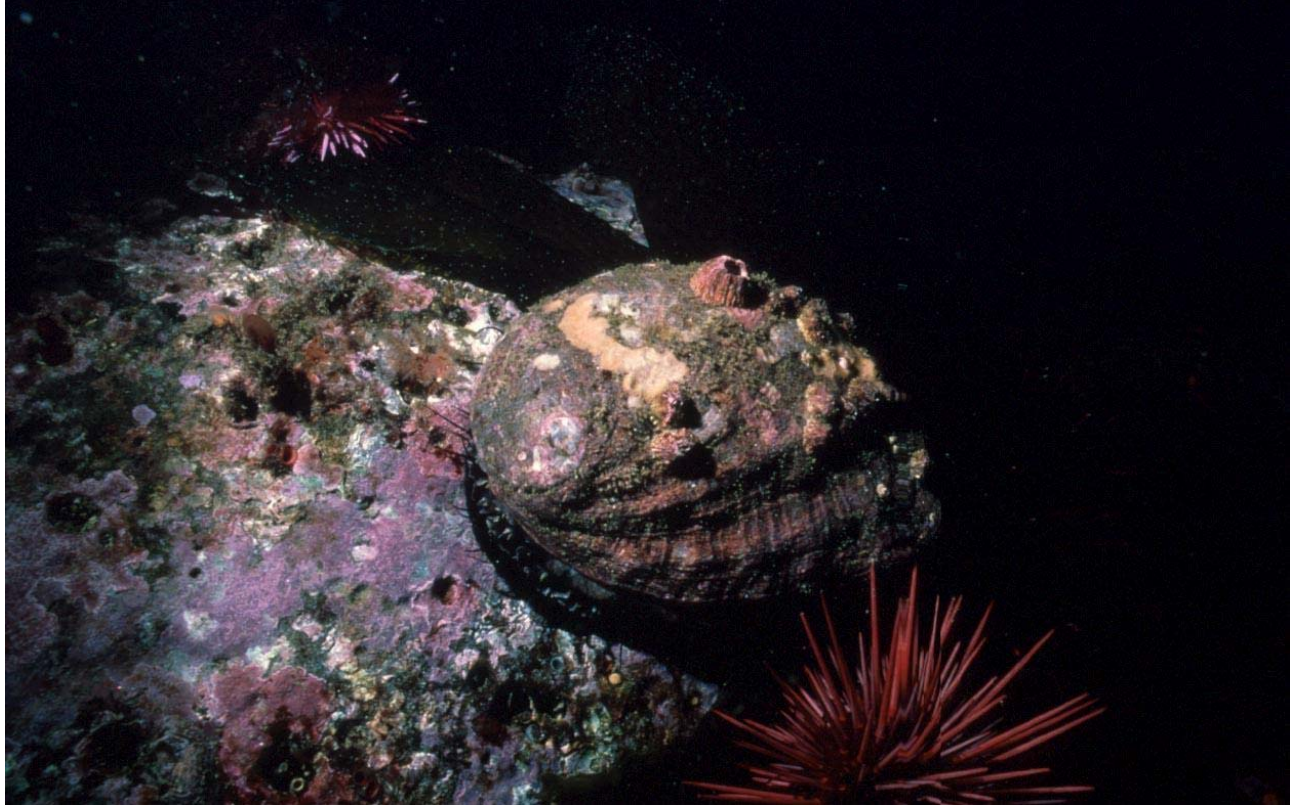


**Ocean Acidification and the Channel Islands National Marine Sanctuary:
*Cause, effect, and response***



Red abalone, urchins, and coralline algae—familiar calcifiers of the Northern Channel Islands. Photo: CINMS

A report by the Conservation Working Group of the CINMS Advisory Council

Adopted by the CINMS Advisory Council September 19, 2008

Prepared by:

Shiva Polefka, Marine Conservation Analyst, and Julia Forgie, Program Intern,
Environmental Defense Center, Santa Barbara, California (contact: shiva@edcnet.org)

Project director:

Linda Krop, CINMS Advisory Council Conservation Seat and Chief Counsel,
Environmental Defense Center

Supported by the Marisla Foundation

Ocean Acidification and the Channel Islands National Marine Sanctuary: *Cause, effect, and response*

Increased acidification of the Earth's ocean water could have far-reaching impacts on the health of our marine environment, and on the long-term sustainability of ecosystems that support human populations. The acidity of the surface oceans has increased by about 30% over the past 200 years, providing clear evidence for ocean acidification on a global scale. As humans continue along the path of CO₂ sequestration in the surface oceans, the impacts on marine ecosystems will be direct and profound.

The Channel Islands National Marine Sanctuary Report on Ocean Acidification is a comprehensive action plan that I hope will be emulated by the other members the National Marine Sanctuary Program.

- Dr. Richard Feely, NOAA Pacific Marine Environmental Laboratory, Seattle, Washington. December 3, 2008.

The Conservation Working Group (CWG) is an advisory body to the Sanctuary Advisory Council of the Channel Islands National Marine Sanctuary (CINMS), and comprises representatives of regional marine conservation organizations and members of the public. The Sanctuary Advisory Council, a 21-member advisory body, provides community and interagency stakeholder advice to the CINMS Superintendent on a variety of Sanctuary management issues. The opinions and findings of the CWG and the Sanctuary Advisory Council do not necessarily reflect the position of CINMS or the National Oceanic and Atmospheric Administration.

For more information on the CWG and the Sanctuary Advisory Council, visit <http://www.channelislands.noaa.gov/sac/main.html>.

Recommended citation: Conservation Working Group, Channel Islands National Marine Sanctuary Advisory Council. *Ocean Acidification and the Channel Islands National Marine Sanctuary: Cause, effect and response*. Adopted by the CINMS Advisory Council September 19, 2008. Prepared by S. Polefka and J. Forgie, Environmental Defense Center, Santa Barbara, California.

**Ocean Acidification and the Channel Islands National Marine Sanctuary:
*Cause, effect, and response***

Contents

I. Executive Summary and Introduction.....4
a: Project background
b: Issue overview
c: Project objectives

II. The Chemistry of Ocean Acidification.....9
a: Trends in atmospheric CO₂ and ocean pH
b: Chemistry of ocean uptake of atmospheric CO₂
c: Anthropogenic CO₂— its effect on ocean pH and chemical equilibrium
d: Uncertainty in ocean acidification models and predictions

III. Biological Impacts.....20
a: Overview
b: Examples of potentially impacted organisms

IV. Ecosystem Effects.....30
a: Overview
b: Changes in and around CINMS

V. Recommendations for CINMS.....33
1: Research
2: Monitor
3: Educate
4: Lead

Appendix 1.....37
NOAA-observed trends in atmospheric CO₂ and ocean pH

Appendix 2.....40
Example marine fauna responses to ocean acidification

Works Cited.....42

I. Executive Summary and Introduction

Unabated CO₂ emissions over the coming centuries may produce changes in ocean pH that are greater than any experienced in the past 300 million years, with the possible exception of those resulting from rare, catastrophic events in Earth's history.

- Ken Caldeira and Michael Wickett¹

a: Project background

Designated in 1980, the Channel Islands National Marine Sanctuary (CINMS or “the Sanctuary”) encompasses 1,128 square nautical miles from the Mean High Water Line to approximately six nautical miles (NM) offshore of the five northern Channel Islands—Santa Barbara, Anacapa, Santa Cruz, Santa Rosa, and San Miguel Islands, as well as Richardson Rock and Castle Rock.²

Because it harbors “an exceptionally rich and diverse biota,”³ CINMS is one of 14 sites overseen by the National Marine Sanctuary Program (NMSP), authorized by Congress to “identify, designate, and manage areas of the marine environment of special national, and in some cases international, significance due to their conservation, recreational, ecological, historical, research, educational, or aesthetic qualities.”⁴ Congress ordered the NMSP to “maintain the natural biological communities” of designated Sanctuaries, and “to protect and, where appropriate, restore and enhance the natural habitats, populations, and ecological processes.”⁵ Based on these mandates, the stated primary purposes of CINMS designation and resource management are “preserving and protecting this unique and fragile ecological community.”⁶

Of course, the physical and biological resources of the Sanctuary are not confined within those boundaries, but flow, drift and move in and out of them. Many species found within the Sanctuary and Santa Barbara Channel (SBC, or “the Channel”) arrive here after traveling hundreds or even thousands of miles, and the area’s ocean waters and meteorological systems gyrate, ebb and flow in cycles of far greater scale than the Sanctuary’s 1,128 square NM.

Similarly, human activities that occur beyond the Sanctuary’s geographic boundaries— and the reach of its protective regulations— yield consequences that can adversely impact its natural resources and qualities.

Global anthropogenic emissions of greenhouse gases (GHG), particularly carbon dioxide (CO₂), perhaps best exemplify this predicament. Broad consensus exists among scientists that these emissions will have worldwide effects on global climate and natural systems, and that, in the decades ahead, emissions and effects will increase. Specifically, in its comprehensive survey of existing research, the Intergovernmental Panel on Climate Change (IPCC) reports the following conclusions:

¹ Caldeira, K., and M.E. Wickett. 2003. “Anthropogenic carbon and ocean pH.” *Nature* 425:365.

² 72 Fed. Reg. 29214, May 24, 2007.

³ *Id.*, p. 29214.

⁴ 15 CFR 922.2(a).

⁵ 16 U.S.C. 1431(b)(3).

⁶ 45 Fed. Reg. 65198, October 2, 1980.

- “Global atmospheric concentrations of CO₂... have increased markedly as a result of human activities since 1750 and now far exceed pre-industrial values... The atmospheric concentrations of CO₂... in 2005 exceed by far the natural range over the last 650,000 years. Global increases in CO₂ concentrations are due primarily to fossil fuel use, with land-use change providing another significant but smaller contribution.”⁷;
- “Most of the observed increase in global average temperatures since the mid-20th century is very likely due to the observed increase in anthropogenic GHG concentrations”⁸;
- “It is likely that anthropogenic warming over the last three decades has had a discernible influence on many natural systems”⁹;
- “With current climate change mitigation policies and related sustainable development practices, global GHG emissions will continue to grow over the next few decades”¹⁰;
- “The uptake of anthropogenic carbon since 1750 has led to the ocean becoming more acidic with an average decrease in pH of 0.1 units. Increasing atmospheric CO₂ concentrations lead to further acidification.”¹¹

The IPCC goes on to state that these global patterns will cause severe localized impacts, stating that, because of global warming, ocean acidification and other human disturbances, “The resilience of many ecosystems is likely to be exceeded this century.”¹²

Because of a growing awareness that the Channel Islands ecosystem could be one of those jeopardized by these dynamics, Sanctuary staff, its interagency resource management partners, and public stakeholders have grown increasingly concerned about anthropogenic GHG emissions, particularly carbon dioxide, and how they could affect Sanctuary resources and qualities.

To act on this concern, the CINMS Advisory Council (SAC) identified ocean acidification as a priority topic for research and the development of an assessment report in its 2008 Work Plan.¹³ Given that the SAC has already advanced recommendations to the CINMS Superintendent (in 2005) to more carefully monitor and study the effects of deposition of airborne pollutants in Sanctuary waters,¹⁴ this prioritization meshes with existing SAC consensus. However, the global scale of the causes and significant effects of ocean acidification represent a distinct and seemingly confounding challenge to the relatively limited jurisdiction of the CINMS, necessitating focused and dedicated study. This report aims to fulfill that necessity.

⁷ IPCC, 2007: Climate Change 2007: Synthesis Report. Contribution of Working Groups I, II and III to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change [Core Writing Team, Pachauri, R.K and Reisinger, A. (eds.)]. IPCC, Geneva, Switzerland, 104 pgs. p. 37.

⁸ *Id.*, p. 38.

⁹ *Id.*, p. 41.

¹⁰ *Id.*, p. 44.

¹¹ *Id.*, p. 52.

¹² *Id.*, p. 48.

¹³ CINMS Sanctuary Advisory Council 2008 Work Plan. Adopted March 14, 2008. Available at <http://channelislands.noaa.gov/sac/pdf/2008WPF.pdf> (viewed May 1, 2008).

¹⁴ Polgar, S., S. Polefka, and A. Eastley. 2005. *A Water Quality Needs Assessment for the Channel Islands National Marine Sanctuary*. Adopted by the Sanctuary Advisory Council on September 23, 2005. Available at: <http://www.channelislands.noaa.gov/sac/pdf/10-17-05.pdf> (viewed May 2, 2008).

b: Issue overview

The world's oceans have absorbed, or taken up, approximately 50% of the carbon dioxide (CO₂) emitted by human fossil fuel burning and cement production over the last 200 years.¹⁵ Without this sink, atmospheric CO₂ levels would be significantly higher, leading to more rapid climate change than that already underway. Oceanic CO₂ uptake results in chemical changes in seawater, and directly impacts the calcification cycle and the ocean's array of calcifying organisms. Rising atmospheric CO₂ levels correspond to a higher CO₂ concentration ([CO₂]¹⁶) in the ocean, and, consequently, a lower carbonate ion concentration ([CO₃²⁻]), a higher hydrogen ion concentration ([H⁺]), and an increase in acidity and in the corrosiveness of the oceans' waters. These changes are embodied in a decrease in measured pH levels in seawater around the world.

Known as "ocean acidification", this chemical process directly results in both reduction of certain marine calcifying organisms' ability to make calcium carbonate (CaCO₃) shells for survival (e.g. coral, coralline algae and urchins), and the dissolution of already existing shells (e.g. pteropods, an ecologically significant group of planktonic swimming snail species).¹⁷ Other biological effects of decreasing ocean water pH have been noted, including hypercapnia, a condition caused by excessive CO₂ in the blood, in fish and cephalopods (e.g. squids)¹⁸, adverse impacts to reproduction, metabolism and growth in some invertebrates¹⁹, and beneficial²⁰ and adverse²¹ impacts to various photosynthetic organisms.

The pH of seawater has long been identified as a key variable in water quality. The U.S. Environmental Protection Agency (EPA) *Quality Criteria for Water* states: "For open ocean waters where the depth is substantially greater than the euphotic zone [commonly defined as the depth to which enough sunlight penetrates to allow for photosynthesis], the pH should not be changed more than 0.2 units outside the range of naturally occurring variation..."²² More recently, as anthropogenic CO₂ emissions continue to climb, Ken Caldeira of the Carnegie Institution for Science reports that, "Atmospheric CO₂ concentrations need to remain at less than 500 parts per million for the ocean pH decrease to stay within the 0.2 limit set forth by the US EPA."²³ Yet according to the IPCC models, that

¹⁵ Royal Society, 2005. *Ocean Acidification due to Atmospheric Carbon Dioxide*. Working Group members: Raven, J., K. Caldeira, H. Elderfield, O. Hoegh-Guldberg, P. Liss, U. Riebesell, J. Shepherd, C. Turley, A. Watson. The Royal Society, London. 68 pgs. Available at: <http://www.royalsoc.ac.uk> (viewed May 2, 2008). p. vi.

¹⁶ In this report, the concentration of a given compound in seawater solution is denoted by bracketing the chemical formula of the compound. For example, "carbon dioxide concentration" will be written as [CO₂].

¹⁷ Orr, J.C., V. J. Fabry, O. Aumont, L. Bopp, S. C. Doney, R. A. Feely, A. Gnanadesikan, N. Gruber, A. Ishida, F. Joos, R. M. Key, K. Lindsay, E. Maier-Reimer, R. Matear, P. Monfray, A. Mouchet, R. G. Najjar, G. Plattner, K. B. Rodgers, C. L. Sabine, J. L. Sarmiento, R. Schlitzer, R. D. Slater, I. J. Totterdell, M. Weirig, Y. Yamanaka, and A. Yool. 2005. "Anthropogenic ocean acidification over the twenty-first century and its impact on calcifying organisms." *Nature* 437:681-686.

¹⁸ *Id.*, p. 19.

¹⁹ *Id.*, pgs. 19-20.

²⁰ *Id.*, p. 18.

²¹ Personal communication, Dr. Gretchen Hofmann, February 27, 2008. Dr. Hofmann reported that preliminary, unpublished data from a study on kelp suggest adverse impacts to certain life stages of the organism.

²² U.S. Environmental Protection Agency. *Quality Criteria for Water* 1976.

²³ Carnegie Institution for Science. "CO₂ emissions could violate EPA ocean-quality standards within decades." Press Release, September 29, 2007.

level of CO₂ could be reached within the next approximately 50 years if CO₂ emissions continue to increase at current rates.²⁴ This prediction essentially encapsulates the issue: carbon emissions from current human activities appear very likely to cause significant degradation of global ocean water quality, and our growing understanding of the potential adverse biological effects suggest that significant changes to marine biological populations and their communities could result.

In addition, while large scale modeling currently predicts average ocean pH to change significantly in the scale of decades, substantial uncertainty exists about the temporal dimension of pH change in the CINMS region specifically. For example, human CO₂ emissions are considered the cause of a significant change in water chemistry (pH and carbonate concentration) that has already occurred in the surface waters of an area offshore northern California.²⁵ Given that physical oceanographic features like upwellings are now documented to be causing acute local effects on the West Coast, CINMS resources and qualities could begin to be affected by ocean acidification within a time scale much shorter than decades.

While much additional research is needed to fully understand the rate of change of local ocean chemistry, and the biological and ecological implications of these changes within the Channel Islands region, the certainty of our understanding of the environmental chemistry driving ocean acidification indicates that long term conservation of CINMS resources and qualities will necessitate taking immediate action to address this global problem.

c: Project objectives

This report aims to catalyze an appropriate local response to ocean acidification through raising awareness and understanding of the issue among CINMS stakeholders, staff, and the public, and by identifying and articulating appropriate actions that these parties can take to prepare for and reduce the effects of ocean acidification on Sanctuary resources.

The SAC Conservation Working Group, in partnership with the Commercial Fishing Working Group, assumed responsibility for this project based on their shared commitment to maintain the long term resilience and productivity of the Sanctuary's marine ecosystem, and because they view ocean acidification as a direct, long term threat to Sanctuary resources that defies traditional regulatory or enforcement-based response.

This report provides an overview of ocean acidification based on a review of scientific research. It examines both the effects of rising atmospheric CO₂ levels on ocean chemistry, and compiles information on known impacts of lowered pH to certain marine organisms. Further, it explores the nascent body of data on potential impacts to ecosystems from changing water chemistry, and discusses the potential impacts to the qualities and resources of the Channel Islands region suggested by this collection of information.

²⁴ Meehl, G.A., T.F. Stocker, W.D. Collins, P. Friedlingstein, A.T. Gaye, J.M. Gregory, A. Kitoh, R. Knutti, J.M. Murphy, A. Noda, S.C.B. Raper, I.G. Watterson, A.J. Weaver and Z.-C. Zhao. 2007: Global Climate Projections. In: *Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change* [Solomon, S., D. Qin, M. Manning, Z. Chen, M. Marquis, K.B. Averyt, M. Tignor and H.L. Miller (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.

²⁵ Feely, R.A., C.L. Sabine, J.M. Hernandez-Ayon, D. Ianson, and B. Hales. 2008. "Evidence for upwelling of corrosive 'acidified' water onto the Continental Shelf." *Science* 320: 1490–1492, doi: 10.1126/science.1155676.

Finally, the report concludes that the magnitude of the problem facing long term conservation of CINMS resources and qualities necessitates four key actions by Sanctuary staff and stakeholders— to *Research*, *Monitor*, *Educate*, and *Lead*, and provides a set of specific recommendations to help advance each one. In summary, the report recommends that CINMS staff and stakeholders—

1. *Research*. CINMS should prioritize the organization of a baseline of physical and biological oceanographic data relevant to understanding the local effects of ocean acidification, systematically identify data gaps and research needs, and begin forming partnerships with researchers and institutions that can illuminate those dynamics and fulfill those needs.
2. *Monitor*. CINMS and its research partners should create an organizational framework to *track changes* in acidification-related physical and biological indicators over time, including how the Sanctuary’s calcifying species and their ecosystems are affected by changes in pH and carbonate saturation.
3. *Educate*. CINMS should use its existing education and outreach programs to help increase awareness of ocean acidification among Sanctuary stakeholders and the public. Content should include the causes of ocean acidification, its effects on Sanctuary resources, qualities and ecosystems, and actions that the public and stakeholders can take to reduce their contribution to ocean acidification.
4. *Lead*. CINMS staff should seize the opportunity to address ocean acidification through leadership among local ocean users, the public, and within the National Marine Sanctuary Program and NOAA. CINMS leadership actions are needed in two areas, (a) CO₂ emissions reduction, and (b) management planning and coordination.

II. The Chemistry of Ocean Acidification

a: Trends in atmospheric CO₂ and ocean pH

Current atmospheric CO₂ concentration is approximately 385 parts per million volume (ppmv)²⁶, an increase of about 100 ppmv since pre-industrial times²⁷ (see [Appendix I](#) for NOAA's recent global CO₂ estimates). This concentration is expected to continue rising by approximately 2ppmv per year over the next few decades as a result of fossil fuel burning and other human activities.²⁸ Atmospheric CO₂ levels would be significantly higher without carbon sinks such as the oceans and terrestrial vegetation. According to Henry's Law,²⁹ the concentration of dissolved CO₂ in the oceans must be in equilibrium with atmospheric CO₂ levels. Therefore, as CO₂ levels in the atmosphere increase, the ocean must absorb, or take up, an increasing amount of the substance. The rate of uptake will decrease in the next decades, as explained below, but the total quantity absorbed will continue to increase. According to the Royal Society (the United Kingdom's national academy of sciences), about half of the total fossil fuel carbon released since pre-industrial times has been taken up by the oceans.³⁰ In another extensive literature survey, Kleypas et al. report on current uptake patterns:

Over the two decades of the 1980s and 1990s only about half of the CO₂ released by human activity has remained in the atmosphere, with the oceans having taken up about 30% and the terrestrial biosphere 20%.³¹

They continue, noting that within a current global context in which “the rate of current and projected [atmospheric] CO₂ increase is about 100x faster than has occurred over the past 650,000 years,” and “the rising atmospheric CO₂ levels are irreversible on human timescales,” over the next millennium the oceans will have absorbed approximately 90% of anthropogenic CO₂ emissions.³²

This ongoing uptake of anthropogenic CO₂ results in increased ocean acidity, signified by a drop in seawater pH; as the level of dissolved CO₂ increases in seawater, the concentration of hydrogen ions ([H⁺]) increases, which reduces the pH of seawater.³³

²⁶ Tans, P., NOAA Earth System Research Laboratory, Global Monitoring Division. “Recent Global Monthly Mean CO₂.” September 2008. Available at <http://www.esrl.noaa.gov/gmd/ccgg/trends/> (viewed September 9, 2008).

²⁷ Division of Atmospheric Research, CSIRO, Aspendale, Victoria, Australia, Laboratoire de Glaciologie et Geophysique de l'Environnement, Saint Martin d'Herès-Cedex, France, and Antarctic CRC and Australian Antarctic Division, Hobart, Tasmania, Australia. June 1998. “Historical CO₂ record derived from a spline fit (20 year cutoff) of the Law Dome DE08 and DE08-2 ice cores.” <http://cdiac.ornl.gov/ftp/trends/co2/lawdome.smoothed.yr20> (Viewed September 9, 2008.)

²⁸ IPCC 2007. p. 37

²⁹ Henry's Law states that at a constant temperature, the amount of a given gas dissolved in a given type and volume of liquid is directly proportional to the partial pressure of the gas in equilibrium with that liquid. See, e.g., Atkins, P. and L. Jones. 1999. *Chemical Principles: The Quest for Insight*. W.H. Freeman and Company, New York. 908 pgs. p. B14.

³⁰ Royal Society. 2005. p. iv.

³¹ Kleypas, J.A., R.A. Feely, V.J. Fabry, C. Langdon, C.L. Sabine, and L.L. Robbins. 2006. *Impacts of Ocean Acidification on Coral Reefs and Other Marine Calcifiers: A Guide for Future Research*. Report of a workshop held 18–20 April 2005, St. Petersburg, FL, sponsored by NSF, NOAA, and the U.S. Geological Survey. 88 pgs. p.3.

³² *Id.*

³³ pH is defined qualitatively as a measurement of the concentration of hydrogen ions (denoted as [H⁺]) in a solution. It is defined quantitatively as follows: $\text{pH} = -\log_{10} [\text{H}^+]$.

While the pH of distilled water is 7.0, the pH of unaltered ocean water varies regionally from 8.0 to 8.3—it is naturally basic.³⁴ Since the advent of industrialization, the average pH of the ocean's surface waters has dropped by approximately 0.1 due to anthropogenic CO₂ emissions (because of the logarithmic basis for pH measurement, this drop corresponds to an approximately 30% increase in concentration of H⁺ ions in the world's oceans)³⁵. Consequently, this phenomenon of CO₂ absorption and elevating H⁺ concentration is termed “ocean acidification.” Recent scientific research, modeling and analysis clearly indicate a further drop in the pH of 0.3-0.5 by the end of the 21st century if present anthropogenic influence continues.³⁶

Preeminent researchers are largely in agreement that this magnitude and rate of change is very significant, even in the Earth's geologic time scale. Caldeira states that “unabated CO₂ emissions over the coming centuries may produce changes in ocean pH that are greater than any experienced in the past 200 million years, with the possible exception of those resulting from rare, catastrophic events in Earth's history.”³⁷ According to the Royal Society, this predicted decrease in ocean pH “is probably lower than has been experienced for hundreds of millennia and, critically, this rate of change is probably one hundred times greater than at any time over this period.”³⁸

b: Chemistry of ocean uptake of atmospheric CO₂

Close examination of the physical process by which accumulating anthropogenic, atmospheric CO₂ lowers ocean pH illustrates both the relatively straightforward nature of ocean acidification, and its inexorability. However, several intermediate reactions must be described to understand the complete process.

First, it's helpful to consider the cycle of carbon dioxide exchange between the ocean and the atmosphere assuming no anthropogenic input of additional CO₂ or other changes arising from purely geological factors. In this idealized scenario, all reactions are in equilibrium, i.e. each reaction proceeds both forward and backward at the same rate. Consequently, there is no net change in the concentrations of substances dissolved in the ocean water.

Each reaction has an equilibrium constant, denoted as *K*, which determines the relative concentrations of the dissolved substances based on the quantity and character of

³⁴ Doney, Scott C. 2006. “The Dangers of Ocean Acidification.” *Scientific American* 294: 58-65. P.61.

³⁵ Royal Society 2005. P.1 One explanation of the mathematics of logarithmic measurement is as follows: “The pH scale is an inverse logarithmic representation of hydrogen ion (H⁺) concentration. Unlike linear scales, which have a constant relationship between the item being measured and the value reported, each individual pH unit is a factor of 10 different than the next higher or lower unit of (H⁺) concentration. For example, a change in pH from 2 to 3 represents a 10-fold decrease in H⁺ concentration, and a shift from 2 to 4 represents a one-hundred (10 × 10)-fold decrease in H⁺ concentration.” Wikipedia. “pH”. <http://en.wikipedia.org/wiki/pH>. (Viewed May 5, 2008).

³⁶ Caldeira, K., and M. E. Wickett. 2005. Ocean model predictions of chemistry changes from carbon dioxide emissions to the atmosphere and ocean. *J. Geophysical Research*, 110, C09S04, doi:10.1029/2004JC002671.

³⁷ Caldeira and Wickett 2003.

³⁸ The Royal Society 2005.

reagents (reacting chemicals), as well as physical variables such as pressure and temperature.³⁹

A key feature of a system in equilibrium is that when the concentration of one reactant changes, the reaction shifts in the direction needed in order to restore the system to its state before the perturbation. For instance, if the compounds on one side of an equation are added or removed by some external system or action, the reaction equilibrium will shift left or right to compensate for the change, until equilibrium is restored. This phenomenon is known as Le Chatelier's Principle⁴⁰, and is central to understanding the role of anthropogenic CO₂ in the ocean's chemistry and carbon cycle.

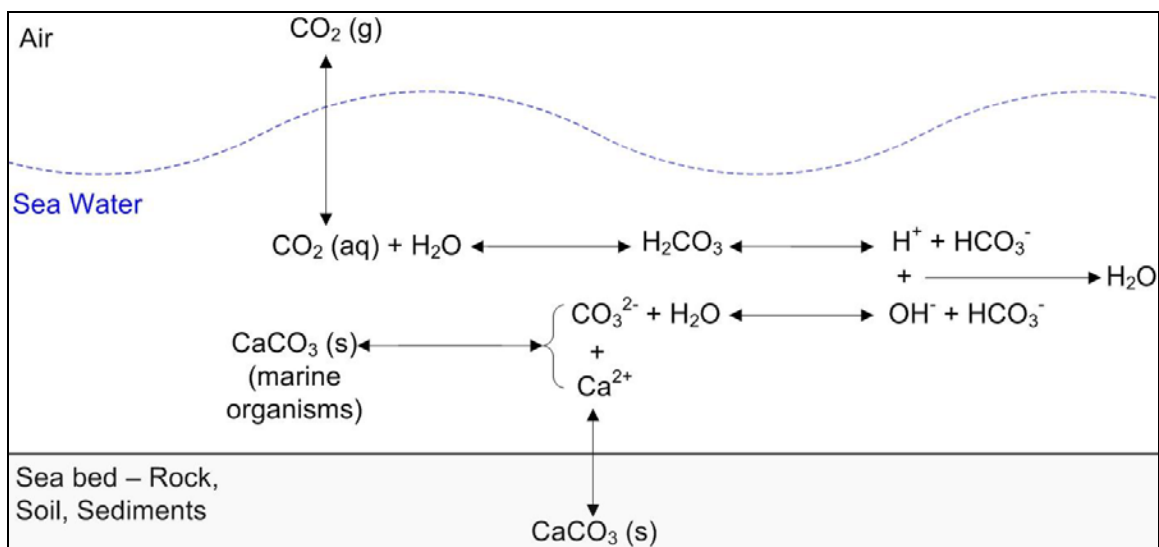


figure 1: Carbonate chemistry in seawater: A simplified model of the multiple chemical reactions that determine the production and concentration of dissolved inorganic carbon and calcium carbonate (CaCO₃) in the ocean.⁴¹

Three forms of inorganic carbon constitute the ocean's total dissolved inorganic carbon (DIC), and exist in the following proportions: CO₂ (1%); bicarbonate ions (HCO₃⁻) (91%), and carbonate ions (CO₃²⁻) (8%).⁴² When dissolved CO₂ in sea water (known as *aqueous* (aq) CO₂) is in equilibrium with atmospheric CO₂, the ongoing reaction is described

³⁹ The equilibrium constant, K, for a reaction is commonly defined as equal to the product of the concentrations of products divided by the product of the concentrations of reactants, with each concentration raised to a power corresponding to the stoichiometry of that compound in the balanced reaction.

⁴⁰ Le Chatelier's Principle is commonly summarized as follows: *If a chemical system at equilibrium experiences a change in concentration, temperature, volume, or total pressure, then the equilibrium shifts to partially counter-act the imposed change.*

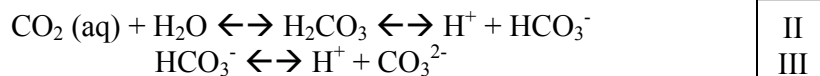
⁴¹ Adapted from *Environmental Chemistry, Third Edition*. Colin Baird and Michael Cann, W.H. Freeman and Company, New York, 2005.

⁴² Schubert, R., H.-J. Schellnhuber, N. Buchmann, A. Epiney, R. Grießhammer, M. Kulesa, D. Messner, S. Rahmstorf, J. Schmid. 2006. *The Future Oceans: Warming up, Rising High, Turning Sour*. German Advisory Council on Global Change, Special Report. Berlin. 123 pgs. Available at: http://www.wbgu.de/wbgu_home_engl.html (Viewed September 12, 2008).

by the following equation, in which the rates at which CO₂ migrates from gas to liquid, and from liquid back to gas, are identical:⁴³



However, dissolved CO₂ in the ocean reacts with seawater to drive several additional chemical processes. First, it forms carbonic acid (H₂CO₃), which in turn partially dissolves to produce a hydrogen ion (H⁺) and a bicarbonate ion (HCO₃⁻). The HCO₃⁻ may further dissociate to form another H⁺ and a carbonate ion (CO₃²⁻). Each of these reactions proceeds forward or backward, to maintain equilibrium.



Although some bicarbonate ions (HCO₃⁻) will dissociate further into carbonate (CO₃²⁻) and hydrogen ions (H⁺) (as shown in equation III), the equilibrium state for this reaction lies far to the left, toward the production of bicarbonate (HCO₃⁻) ions. Therefore, this reaction can be understood as the additional formation of HCO₃⁻ from the reaction of CO₃²⁻ with produced hydrogen ions.

In simplified form, the net reaction for the three intermediate steps (reactions I, II and III) above is:



In other words, as anthropogenic, dissolved CO₂ is forced into the system, it responds by extracting ambient carbonate (CO₃²⁻) and producing more bicarbonate (HCO₃⁻, at a rate of two molecules for every one molecule of the other three species), in order to restore equilibrium per Le Chatelier's Principle.

The CO₃²⁻ in this reaction originates from the shells and other hard structures of many organisms in the ocean, which are composed of calcium carbonate (CaCO₃). Abundant CaCO₃ is also found in subsea geological formations and sediments. Three main forms of crystalline CaCO₃ persist in the ocean, distinguished by their molecular structures and additional element content: aragonite maintains an orthorhombic symmetry in its structure (roughly, a matrix of molecules characterized by rectangular cubes), and normal calcite, and high-magnesium (Mg) calcite, have a trigonal structure (a rhombus-based matrix, like a stack of skewed cubes).⁴⁴

Aragonite and high-Mg calcite are more soluble than normal calcite, which means they will dissolve and dissociate into their component ions— calcium (Ca²⁺) and carbonate (CO₃²⁻)— more readily.⁴⁵

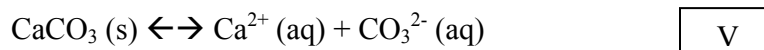
⁴³ The following examination of chemical reactions is summarized from: McElroy, Michael B. 2002. *The Atmospheric Environment: Effects of Human Activity*. Princeton University Press, Princeton, New Jersey. 360 pgs.

⁴⁴ Doney 2006; The Royal Society 2005.

⁴⁵ Doney 2006.

Thus, marine organisms possessing shells composed of these types of CaCO₃ are more susceptible to dissolution when exposed to a lower pH environment.

When CaCO₃ shells dissolve, they dissociate into their component ions according to the following equation:⁴⁶



The equilibrium constant in this reaction is known as the *apparent solubility product constant*, K_{sp} , and is approximated as the product of the concentrations of the dissolved component ions when they are saturated (at equilibrium) in a solution⁴⁷:

$$K_{\text{sp}} = [\text{Ca}^{2+}] \times [\text{CO}_3^{2-}]. \quad \boxed{\text{VI}}$$

As a measured physical value, K_{sp} has a numerical value dependent on the pressure and temperature of the solution. For example, K_{sp} for calcium carbonate is reported as 8.7×10^{-9} at 25°C (as mentioned above, equilibrium depends on pressure and temperature).⁴⁸

Depending on the concentrations of Ca²⁺ and CO₃²⁻ ions in a given volume of seawater, the reactions in equation V will either produce a net precipitation of solid calcium carbonate (CaCO₃), or a net dissolution of the compound into the constituent ions, according to the laws of chemical equilibrium described earlier. If the reaction is initially in equilibrium, and the concentration of CO₃²⁻ subsequently decreases (for example, through increased production of bicarbonate (HCO₃⁻) in the process described above), the reaction equilibrium of equation V will shift to the right, increasing the dissolution of CaCO₃.

To understand the point at which the reaction shifts direction in a given volume of solution, scientists rely on a calculation of the *saturation state*, denoted as Ω (omega), and define it as the product of the actual measured concentrations of the dissolved constituent ions in a solution, divided by the *apparent solubility product* described above. Thus, for calcium carbonate, the saturation state would be calculated as follows:

$$\Omega = [\text{Ca}^{2+}] \times [\text{CO}_3^{2-}] / K_{\text{sp}} \quad \boxed{\text{VII}}$$

The higher the Ω value, the more precipitation is promoted; the lower the Ω value, the more dissolution of calcium carbonate into its components is promoted.⁴⁹ For example, according to Feely et al., in oceanic regions where Ω for aragonite or calcite is greater than 1.0, formation of shells and other biological hard parts are favored, but “below a value of 1.0

⁴⁶ McElroy 2002.

⁴⁷ Atkins and Jones 1999. p. B26-7.

⁴⁸ Id.

⁴⁹ Feely, R. A., C. L. Sabine, K. Lee, W. Berelson, J. Kleypas, V. J. Fabry, and F. J. Millero. 2004. “Impact of Anthropogenic CO₂ on the CaCO₃ System in the Oceans.” *Science* 305: 362-6. Feely et al. (2004) provide a technically accurate definition of degree of saturation for calcium carbonate, Ω , as follows: “the ion product of the concentrations of calcium and carbonate ions, at the in situ temperature, salinity, and pressure, divided by the apparent solubility product (K^*_{sp}) for those conditions.”

the water is corrosive and dissolution of... unprotected aragonite shells will begin to occur.”⁵⁰

Shallow, warm water regions of the ocean, which have a high concentration of CO_3^{2-} ions, are said to be “supersaturated.” This means that they have a higher Ω , and thus will not promote dissolution of CaCO_3 . In contrast, “undersaturated” deep, cold water regions have a lower concentration of CO_3^{2-} and therefore promote dissolution of CaCO_3 and inhibit its precipitation. In a given column of sea water, the transition zone between these two regions is known as the *saturation horizon*.⁵¹ This marks the point below which CaCO_3 will dissolve because there is no longer an adequate concentration of CO_3^{2-} ions to promote the calcium carbonate precipitation (such as shell building).⁵² Seawater is considered to be supersaturated with respect to aragonite when carbonate ion concentration ($[\text{CO}_3^{2-}]$) is greater than approximately 66 micromols⁵³ per kilogram of sea water solution ($\mu\text{mol/kg}$).⁵⁴ Currently, global peaks in $[\text{CO}_3^{2-}]$, at approximately 240 $\mu\text{mol/kg}$, are found in the tropics. In contrast, the Southern Ocean averages 105 $\mu\text{mol/kg}$.

c: Anthropogenic CO_2 — its effect on ocean pH and chemical equilibrium

Anthropogenic emissions of CO_2 at the rates occurring since industrialization cause a significant perturbation to the system of interdependent reactions described above, pushing it out of equilibrium. First, additional atmospheric CO_2 will shift reaction (I) to the right, forcing increased uptake of CO_2 by the oceans. Additional dissolved CO_2 will subsequently force reaction (II) to the right, resulting in increased production of bicarbonate (HCO_3^-) and hydrogen ions (H^+). Additional H^+ ions in the water force reaction (III) further to the left, causing production of even more bicarbonate (HCO_3^-). The increase H^+ concentration will drive reaction (III) to the left, causing a net consumption of carbonate ions (CO_3^{2-}) and production of bicarbonate (HCO_3^-). However, not all of the additional H^+ will be consumed in reaction (III). The net result of reactions (II) and (III) is an increase in the concentration of bicarbonate (HCO_3^-), a decrease in that of carbonate (CO_3^{2-}), and an increase in the concentration of H^+ . Consequently, because pH is measured as the negative logarithm of the hydrogen ion concentration (see notes 30 and 32, above), the result is a reduction in seawater pH and an increasingly corrosive ocean.

In simplified form, increased emissions forces CO_2 dissolution into the oceans. Increased $[\text{CO}_2]$ in seawater leads to higher $[\text{H}^+]$ and $[\text{HCO}_3^-]$, lower pH; and greater dissolution of geological and biological calcium carbonate (CaCO_3):

1. $\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{CO}_3^-$
2. $\text{H}_2\text{CO}_3 \rightarrow \text{HCO}_3^- + \text{H}^+$
3. $\text{H}^+ + \text{CO}_3^{2-} \rightarrow \text{HCO}_3^-$

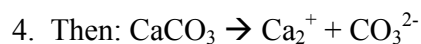
⁵⁰ Feely, R.A., C.L. Sabine, J.M. Hernandez-Ayon, D. Ianson, and B. Hales. 2008. “Evidence for upwelling of corrosive ‘acidified’ water onto the Continental Shelf.” *Science* 320: 1490–1492, doi: 10.1126/science.1155676.

⁵¹ Doney 2006.

⁵² The Royal Society 2005.

⁵³ The “mol” is the international symbol for the counting measure “mole”, which corresponds to Avogadro’s number, approximately 6.022×10^{23} . Moles are simply measures of counting, analogous to a “dozen” or a “score”, though typically applied in chemistry for measurements of molecular concentrations. See, for example, “Mole (unit),” at http://en.wikipedia.org/wiki/Mole_%28unit%29. A micromol is thus one millionth of a mole; i.e. there are one million micromols per mol of that which is being counted.

⁵⁴ Schulbert et al. 2006.



Carbonate (CO_3^{2-}) concentration in seawater has already been reduced worldwide by about 16% since pre-industrial concentrations.⁵⁵ As the “forcing” of anthropogenic CO_2 on the world’s oceans continues to reduce carbonate concentration, the oceans will be able to take up atmospheric CO_2 at a decreasing rate. By some estimates, the change in surface-ocean DIC per unit increase in atmospheric CO_2 could be 60% lower by 2100 than it is today.⁵⁶ Despite this decreasing rate of absorption, the concentration of H^+ ions will continue to increase, causing a steady decrease in ocean pH.

As mentioned, calcium carbonate solubility increases with pressure and decreases with temperature— cold, deep ocean waters are naturally less saturated with respect to carbonate forms like aragonite and calcite, and thus naturally have a lower pH than surface waters. Consequently, polar and deep benthic waters are the most sensitive to anthropogenic forcing of CO_2 , and are understood to have already undergone significant change because of it: carbonate ion (CO_3^{2-}) concentration has already fallen below the saturation horizon in many such areas, meaning that calcium carbonate shells in these areas now tend to dissolve.⁵⁷ This dynamic is further discussed below.

For long-term gradual changes in pH, the ocean’s “carbonate buffer” works to counteract the increase in H^+ ions.⁵⁸ When an acid like CO_2 is added to seawater, some of the H^+ ions react with carbonate (CO_3^{2-}) to form HCO_3^- , as explained in the equations above. However, as more CO_2 is absorbed by the oceans, the buffering capacity diminishes because there is a reduction in the concentration of carbonate (CO_3^{2-}) ions, which are needed for the buffer to function.⁵⁹

Data produced from modeling of CO_2 forcing on oceans completed at Lawrence Livermore National Laboratory suggests that the carbonate buffer functions in scenarios of gradual atmospheric CO_2 change, not the rapid increase underway today.⁶⁰ According to Caldeira (a principal investigator in the modeling study), ocean pH is demonstrated to be “relatively sensitive to added CO_2 ” during short-term, rapid changes in atmospheric CO_2 , whereas long term change (100,000 years) tends to be buffered by carbonate minerals⁶¹ Their study concluded that rapid weakening of the ocean’s carbonate buffer by anthropogenic CO_2 emissions “may produce changes in ocean pH greater than any... in the past 300 million years.”⁶²

Decreased concentrations of carbonate (CO_3^{2-}) adversely impact the precipitation of calcium carbonate (CaCO_3), for example in the production of shells. As a result, there will be more dissolution of calcium carbonate (CaCO_3), whether in subsea geology, or the shells and bodies of marine organisms, and less precipitation of the compound into biological structures. Additionally, reduction of carbonate (CO_3^{2-}) concentration in the world’s oceans mean that

⁵⁵ Kleypas et al. 2006.

⁵⁶ Orr et al. 2005.

⁵⁷ Doney 2006.

⁵⁸ The Royal Society 2005.

⁵⁹ Id.

⁶⁰ Caldeira and Wickett 2003.

⁶¹ Id.

⁶² Id.

fewer regions will be considered “supersaturated” with respect to carbonate minerals. Scientists have already observed an upward shift in saturation horizons around the world because of an overall decrease in $[\text{CO}_3^{2-}]$ ⁶³; since the 19th century it has risen by 50 to 200 meters.⁶⁴ This means that, in some locations, organisms that rely on CaCO_3 precipitation to form their bodies are already experiencing shrinking habitat.

Because aragonite and high-Mg calcite are more soluble than normal CaCO_3 , they have an even shallower saturation horizon, which means an even more acute effect on organisms that depend on precipitation of these forms of the compound.⁶⁵ Guinotte et al. (2006) examined this issue for deep water corals, which depend on aragonite, by overlaying global organism distribution with changes in the aragonite saturation horizon predicted by Orr et al. (2005), and report illustrative findings. For organisms to form aragonite-based shells, the aragonite saturation state (Ω_{arag} , see definition on page 9, above) of the surrounding sea water must be greater than 1.0. According to the researchers, of 410 known deep water coral sites, during pre-industrial times “...95% of the coral locations were found in areas that were supersaturated ($\Omega_{\text{arag}} > 1$). The mean Ω_{arag} value for all coral locations in preindustrial times was 1.98 (supersaturated).”⁶⁶ In contrast,

By 2099, only 30% of [deep water] coral locations remain in supersaturated waters, the vast majority of which are located in the North Atlantic, where the aragonite saturation horizon remains relatively deep.⁶⁷

Mean Ω_{arag} values for all deep water coral locations in 2099 is 0.99 (undersaturated).⁶⁸ As additional context, the Orr et al. (2005) modeling analysis predicts that, under the IPCC’s “business-as-usual” scenario for future anthropogenic CO_2 emissions (IS92a), “some polar and subpolar surface waters will become undersaturated... probably within the next 50 years.”⁶⁹ In this scenario, there would essentially be no saturation horizon for aragonite in these regions, and therefore no place for organisms that rely on aragonitic CaCO_3 shells to form or maintain their bodies. Modeled results show that calcite undersaturation lags behind that of aragonite by only about 50 to 100 years.⁷⁰

Additional modeling studies at Lawrence Livermore Lab by Caldeira and Wickett, in which they forecast ocean pH change under the various future CO_2 emissions scenarios presented and analyzed by the IPCC⁷¹, and various carbon dioxide emissions “stabilization

⁶³ Id.

⁶⁴ Doney 2006.

⁶⁵ Guinotte1, J.M., J. Orr, S. Cairns, A. Freiwald, L. Morgan, and R. George. 2006. “Will human-induced changes in seawater chemistry alter the distribution of deep-sea scleractinian corals?” *Frontiers in Ecology and the Environment* 4(3): 141–146. According to the authors: “The saturation depth for calcite is considerably greater than for aragonite because calcite is less soluble than aragonite in seawater. However, calcitic marine organisms will not be immune from saturation changes in the oceans because the depth of the calcite saturation horizon is also moving progressively shallower over time.” p. 142.

⁶⁶ Id.

⁶⁷ Id.

⁶⁸ Id., pgs. 142-3.

⁶⁹ Orr et al 2005, p. 681.

⁷⁰ Id.

⁷¹ IPCC. 2000. *Special Report on Emissions Scenarios, Working Group III, Intergovernmental Panel on Climate Change*. Edited by N. Nakicenovic et al., 595 pgs., Cambridge Univ. Press, New York.

pathways” evaluated by Wigley, Richels and Edmunds (1996)⁷², further illuminate how these changes will continue into the future. Their results indicate that all four of the IPCC’s major emissions scenarios “produce global surface pH reductions of approximately 0.3–0.5 units by year 2100.” In addition, they determined from their results that, even in a scenario featuring the stabilization of atmospheric CO₂ at 450 ppmv (arguably highly optimistic), that concentration of atmospheric carbon “produces both calcite and aragonite undersaturation in most of the deep ocean.”⁷³

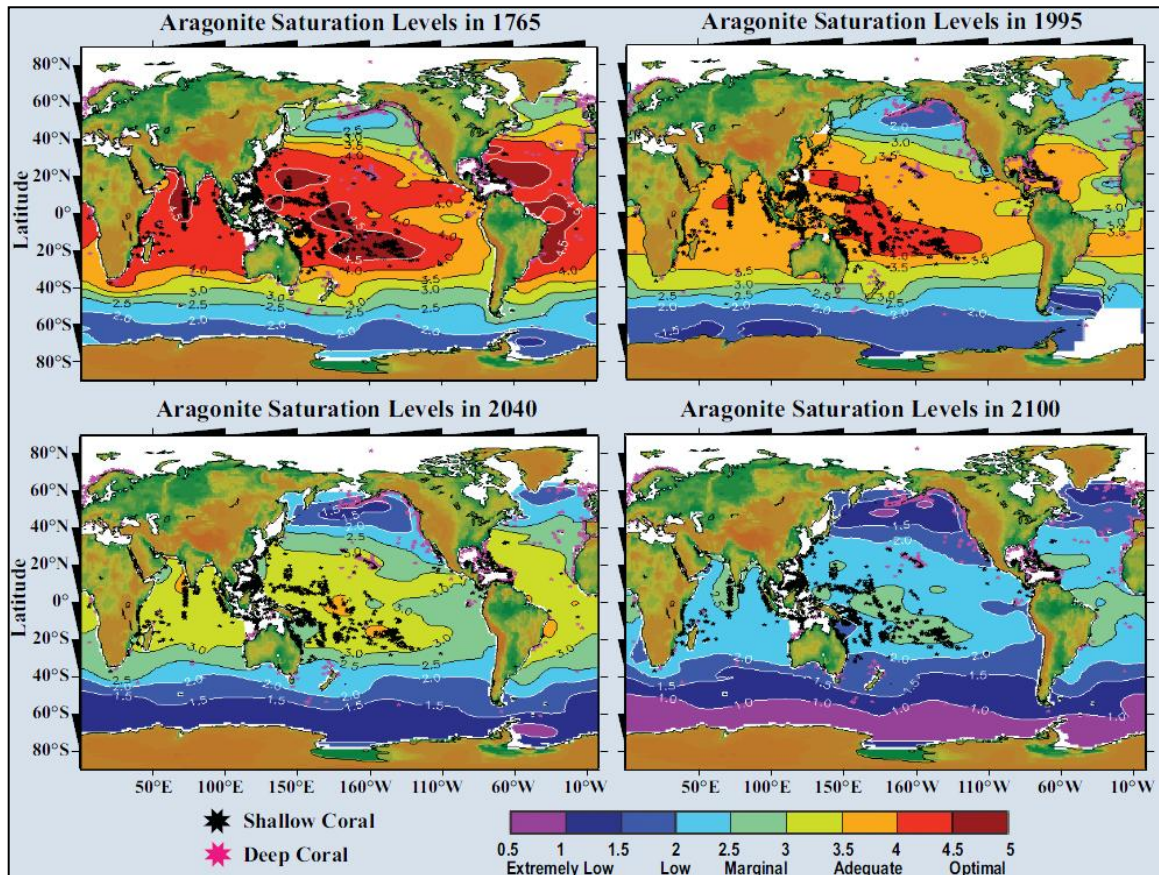


Figure 2: Estimated aragonite saturation states of the surface ocean for the years 1765, 1995, 2040, and 2100 (Feely et al. (2006)⁷⁴, as excerpted from, and cited in, Kleypas et al. (2006)). Kleypas et al. note that this figure’s projections are “based on the modeling results of Orr et al. (2005) and a Business-As-Usual CO₂ emissions scenario,” and that “the distributions of deep-sea coral banks are from Guinotte et al. (2006).”

However, more recent evidence suggests that anthropogenic undersaturation of carbonate is already spreading to lower latitudes and higher reaches of the ocean water column, much faster than predicted in the earlier studies. A series of hydrographic survey cruises in late spring of 2007, led by NOAA researchers and conducted systematically from British Columbia to Southern Baja California, identified shoaling and even surfacing of low-

⁷² Wigley, T., R. Richels, and J. Edmonds. 1996. “Economic and environmental choices in the stabilization of atmospheric CO₂ concentration.” *Nature*, 379: 242–245.

⁷³ Caldeira and Wickett 2005.

⁷⁴ Feely, R.A., J. Orr, V.J. Fabry, J.A. Kleypas, C.L. Sabine, and C. Langdon. (submitted 2006). “Present and future changes in seawater chemistry due to ocean acidification.” AGU Monograph on “The Science and Technology of Carbon Sequestration.”

pH seawater that was undersaturated with respect to aragonite off Cape Mendocino near the California/Oregon border.⁷⁵ In their report, the researchers concluded that their observations “indicate that the upwelling process caused the entire water column shoreward of the 50m bottom contour to become undersaturated with respect to aragonite, a condition that was not predicted to occur in open-ocean surface waters until 2050.”⁷⁶ The team directly addressed the question as to whether their observations were simply those of natural oceanographic variation, or of a human-caused phenomenon. By analyzing the DIC and tracer data collected on previous cruises in the northeastern Pacific, they were able to estimate the anthropogenic component of the carbonate-undersaturated water they sampled. They subsequently made the following conclusion:

...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_2 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_2 .

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.⁷⁷

These results warrant close attention by CINMS resource managers and stakeholders, given that the surfacing of this undersaturated sea water occurred relatively close (in latitude) to the Sanctuary, and because, like the shelf regions off Cape Mendocino where Feely et al. made their observations, the Sanctuary is subject to deep water upwellings.⁷⁸

d: Uncertainty in ocean acidification models and predictions

Certain complicating factors such as temperature and salinity changes, regional and latitudinal variation in CO_3^{2-} concentration, and the effects of water column dissolution and sedimentary processes, reduce the certainty of the predictions for future ocean pH and carbon compound concentrations.⁷⁹ Nonetheless, scientists consider the overall certainty of predictions for ocean chemistry changes given future CO_2 emissions scenarios quite strong relative to the study of other impacts. For example, Orr et al. (2005) state:

For a given atmospheric CO_2 scenario, predicted CO_3^{2-} changes in surface ocean are much more certain than the related changes in climate. The latter depend not only on the model response to CO_2 forcing, but also on poorly constrained physical processes, such as those associated with clouds.⁸⁰

⁷⁵ Feely et al. 2008.

⁷⁶ Id.

⁷⁷ Id.

⁷⁸ NOAA National Centers for Coastal Ocean Science (NCCOS) 2005. *A Biogeographic Assessment of the Channel Islands National Marine Sanctuary: A Review of Boundary Expansion Concepts for NOAA's National Marine Sanctuary Program*. Prepared by NCCOS's Biogeography Team in cooperation with the National Marine Sanctuary Program. Silver Spring, MD. NOAA Technical Memorandum NOS NCCOS 21. 215 pgs, see pgs. 19-20.

⁷⁹ Personal communication, Dr. Richard Feely, NOAA PMEL, via email, August 30, 2008.

⁸⁰ Orr et al. 2005. p. 684.

In addition, key studies have already addressed several major uncertainties directly, and concluded that, other than the future rate of CO₂ emissions, other factors do not have the potential to significantly alter the pH and carbonate dynamics discussed above.

Ocean temperature is the first important example. Increases in temperature shift the equilibrium depicted in reaction (V) to the left, suggesting that in a generally warmer climate, ocean uptake of CO₂ will decrease,⁸¹ bicarbonate concentration ([HCO₃⁻]) will decrease, carbonate concentration ([CO₃²⁻]) will increase, and more CO₂ will be transferred from the oceans to the atmosphere.⁸² Theoretically, global warming could actually thus serve as a slight buffer against decreasing ocean pH. On the other hand, existing data on this topic suggests that the overall effect would likely not meaningfully counteract the chemical impact of rising oceanic [CO₂]. One recent study directly investigating the effect of anthropogenic climate change on acidification concluded that “future changes in ocean acidification caused by emissions of CO₂ to the atmosphere are largely independent of the amounts of climate change.”⁸³ In their large-scale modeling study, Orr et al. (2005) included global ocean warming in their models. The results led them to the following conclusion:

[The] models agree that twenty-first century climate change will cause a general increase in surface ocean CO₃²⁻, mainly because most surface waters will be warmer. However, the models also agree that the magnitude of this increase in CO₃²⁻ is small, typically counteracting less than 10% of the decrease due to the geochemical effect [increasing atmospheric CO₂]. High-latitude surface waters show the smallest increases in CO₃²⁻; and even small reductions in some cases. Therefore, our analysis suggests that physical climate change alone will not substantially alter high-latitude surface CO₃²⁻ during the twenty-first century.⁸⁴

Orr et al. (2005) factored other sources of uncertainty in current predictions. First, they point out that latitude and physical oceanography largely determine the regional oceanic concentration of CO₃²⁻, which can vary by as much as a factor of two in different areas. Its concentration is low in the Southern Ocean because of low surface temperature and large deepwater upwelling, while seasonal variability of temperatures results in an oscillation in [CO₃²⁻].⁸⁵ For instance, they point out that high latitude waters are substantially less saturated with CO₃²⁻ during the winter; however, based on their analysis, they conclude that these effects are also “negligible when compared with the magnitude of the anthropogenic decline.”⁸⁶

The effect that lower ocean pH has on rock and other geological formations has been identified as another source of uncertainty in acidification projections. This too, however, has been evaluated as negligible relative to the magnitude and rate of anthropogenic CO₂ forcing, as Kleypas et al. (2006) conclude in their study:

⁸¹ McElroy 2002., Royal Society 2005.

⁸² The Royal Society 2005; Orr et al 2005.

⁸³ Cao, L., K. Caldeira, and A. K. Jain. 2007. “Effects of carbon dioxide and climate change on ocean acidification and carbonate mineral saturation.” *Geophysical Research Letters*, 34, L05607, doi:10.1029/2006GL028605.

⁸⁴ Orr et al 2005. p.683.

⁸⁵ Id.

⁸⁶ Id.

Ocean alkalinities could have been higher during periods with high CO₂ levels, since higher CO₂ levels accelerate rock weathering and CaCO₃ dissolution, which raises alkalinity. Over long timescales, this feedback tends to maintain a balance between atmospheric CO₂ and oceanic alkalinity. At the current rate of atmospheric CO₂ increase, however, this feedback operates too slowly to raise alkalinity significantly.⁸⁷

Orr et al. (2005) conclude their discussion of uncertainty with a critically important statement on the factor that is overwhelmingly more significant with respect to future changes in ocean pH and carbonate concentration: “The largest uncertainty by far, and the only means to limit the future decline in ocean CO₃²⁻, is the atmospheric CO₂ trajectory.”⁸⁸ That is, the magnitude and rate of future anthropogenic emissions.

Future studies will make the models more accurate and allow for more geographically specific predictions. The surprising results published by Feely et al. (2008) demonstrating clearly that upwelling is already causing significant changes to ocean chemistry in localized areas along the California coast underscore the importance of additional localized study of acidification-related dynamics; this would seem to be particularly salient for ocean areas of significant natural resource and socioeconomic importance like the CINMS.

III. Biological Impacts

Laboratory experiments are now available to show the deleterious effects of increased carbon dioxide (and the lower pH that results) for all the major groups of marine organisms that have hard parts made of calcium carbonate.

- Scott Doney,
Senior Scientist of marine chemistry and geochemistry at Woods Hole
Oceanographic Institution.⁸⁹

a: Overview

The ocean chemistry outlined above describes the effects that result from a human-caused increase in atmospheric CO₂— higher [CO₂], [H⁺] and [HCO₃⁻], and lower [CO₃²⁻], which lower ocean pH. These changes also affect certain marine organisms and their biological communities. Based on their comprehensive review of existing data, Fabry et al. (2008) conclude that “ocean acidification and the synergistic impacts of other anthropogenic stressors provide great potential for widespread changes to marine ecosystems.”⁹⁰

Direct, adverse effects on the physiology of a broad array of calcifying fauna are perhaps the principal impacts of concern with respect to ocean acidification. Calcium carbonate-based structures occur not only as the external shells of mollusks like bivalves and gastropods, but also as the shells of corals, in the exoskeletons of echinoderms like urchins and arthropods like barnacles and lobsters, in the internalized shells of some cephalopods like

⁸⁷ Kleypas et al 2006. p. 6.

⁸⁸ Orr et al 2005. p. 684

⁸⁹ Doney, Scott C. 2006. “The Dangers of Ocean Acidification.” *Scientific American* 294: 58-65. p. 61.

⁹⁰ Fabry, V. J., B.A. Seibel, R.A. Feely, and J.C. Orr. 2008. “Impacts of ocean acidification on marine fauna and ecosystem processes.” *ICES Journal of Marine Science*, 65: 414–432.

squid and cuttlefish (e.g. “cuttlebones”), and in the gravity- and acceleration-sensing organs (otoliths) in fish.

Fabry et al. (2008) effectively summarize the current state of knowledge on biological and ecological changes for fauna due to ocean acidification:

The ability of marine animals, most importantly pteropod molluscs, foraminifera, and some benthic invertebrates, to produce calcareous [calcium carbonate-based] skeletal structures is directly affected by seawater CO₂ chemistry.⁹¹

Increasing CO₂ levels are documented to cause calcareous structures to dissolve, as well as reduce organisms’ ability to grow shells and other structures, according to a broad survey of the relevant literature by Doney (2006).⁹² The Royal Society (2005) concurs with this claim in its own comprehensive literature review, reporting numerous predictions of decreased calcification: “published data on corals... and foraminifera [described below] all suggest a reduction in calcification by 5-25% in response to a doubling of atmospheric CO₂ from pre-industrial values.”⁹³ Kleypas et al. (2006) refer to multiple studies, concluding that “dissolution rates of carbonates will increase in response to increasing concentrations of CO₂. Even small changes in CO₂ concentrations in surface waters may have large negative impacts on marine calcifiers and natural biogeochemical cycles of the ocean.”⁹⁴ This two-pronged threat to marine fauna, of dissolution and reduced calcification, will probably affect different species to varying degrees, influenced by factors such as individual species’ resilience to pH change, geographic location, and adaptation capacity.

CO₂-induced acidification of bodily fluids– hypercapnia– also can affect marine organisms as CO₂ concentrations increase.⁹⁵ In fish, the structure and activity of some cell tissues changes after only twenty four hours of hypercapnia,⁹⁶ though fish in general exhibit significant capacity to buffer their internal pH against changes in the environment.⁹⁷

Hypercapnia from elevated CO₂ levels is documented as directly impacting growth and survival rates in invertebrates, however. Michaelidis et al (2005) studied the effects of lower pH on the Mediterranean mussel *Mytilus galloprovincialis*. At a pH of 7.3, an extremely low level that the researchers cite as “the maximum pH drop expected in marine surface waters during atmospheric CO₂ accumulation,” the mussel suffered reduced growth as well as shell dissolution.⁹⁸ The researchers concluded that their observations “strongly indicate that a reduction in sea-water pH to 7.3 may be fatal for the mussels.”⁹⁹

⁹¹ Id.

⁹² Doney 2006.

⁹³ The Royal Society 2005, citing Feely et al 2004. As noted earlier in the report, IPCC forecasts suggest that this atmospheric carbon concentration is likely to occur within the next 5-7 decades.

⁹⁴ Kleypas et al 2006. Citing Gattuso et al 1998, Wolf-Gladrow et al 1999, Langdon et al 2000, Riebesell et al 2000, Marubini et al 2001, Zondervan et al 2001, Reynaud et al 2003.

⁹⁵ The Royal Society 2005.

⁹⁶ Id.

⁹⁷ Fabry et al. 2008.

⁹⁸ Michaelidis, B., C. Ouzounis, A. Palaras, and H.O. Pörtner. 2005. “Effects of long-term moderate hypercapnia on acid-base balance and growth rate in marine mussels *Mytilus galloprovincialis*.” *Marine Ecology*, Progress Series (Vol. 293).

⁹⁹ Id.

Shirayama and Thornton studied the effects of an additional 200 ppm of atmospheric CO₂ on juveniles of two species of Japanese sea urchin (*Hemicentrotus pulcherrimus* and *Echinometra mathaei*), and one gastropod mollusk (the conch snail *Strombus luhuanus*); they observed significant mortality among the urchins, and decreased growth rates among all three species over the six month long experiment.¹⁰⁰ The researchers noted physiological impacts beyond the adverse effect on calcification, and found that the sea urchins were more acutely affected than the gastropods due to “their inability to regulate changes in their internal body condition.”¹⁰¹

It should be pointed out that both of the above experimental scenarios were highly artificial and of unknown value in predicting how the complex CINMS environment will be affected by acidification. Nonetheless, taken within the context of steadily and rapidly increasing atmospheric [CO₂], the results could be considered a warning of adverse impacts to socioeconomically and ecologically important CINMS species in the absence of some form of adaptation.

While much uncertainty exists about organisms’ ability to adapt to the changing ocean pH, it has been the subject of some research. Seibel and Fabry (2003) predict that reduced calcification would decrease an organism’s ability to survive and force it to shift its latitude or vertical depth habitat range.¹⁰² However, this habitat shift may be impossible for some species, especially when conditions are changing so rapidly relative to the geologic record (as discussed above). Hoegh-Guldberg et al (2007), in their discussion of acidification impacts to corals, emphasize the importance of the current rate of change, suggesting that “the rate of [CO₂] change is critical given that modern genotypes and phenotypes of corals do not appear to have the capacity to adapt fast enough to sudden environmental change.”¹⁰³ Kleypas et al. (2006) state: “There is no experimental evidence from either single organisms or multi-species mesocosms that corals or coralline algae can acclimate or adapt to lowered saturation state.”¹⁰⁴ In contrast, Collins and Bell (2004) studied *Chlamydomonas*, a genus of green algae, grown at three times the present atmospheric CO₂ levels. Under lab conditions, this organism successfully acclimatized without genetic mutation.¹⁰⁵ Again, no serious predictions as to how CINMS biota will be affected or change can be made without completion of a great deal more research on the biota and physical oceanography of the Channel Islands region. However, existing evidence does seem to suggest the potential for significant, long-term changes in Sanctuary communities in the years and decades ahead.

The *Chlamydomonas* results illuminate how, although many marine fauna appear likely to suffer from increasing CO₂ levels, emerging data suggests a more mixed array of effects for marine flora. The Royal Society reports that, for photosynthetic “benthic macro

¹⁰⁰ Shirayama Y., and H. Thornton. 2005. Effect of Increased atmospheric CO₂ on shallow water marine benthos. *Journal of Geophysical Research*, 110. C09S08, doi:10.1029/2004JC002618.

¹⁰¹ *Id.*

¹⁰² Seibel, B.A., and V.J. Fabry. 2003. “Marine biotic response to elevated carbon dioxide.” *Advances in Applied Biodiversity Science* 4, 59–67.

¹⁰³ Hoegh-Guldberg, O. P.J. Mumby, A. J. Hooten, R. S. Steneck, P. Greenfield, E. Gomez, C. D. Harvell, P. F. Sale, A. J. Edwards, K. Caldeira, N. Knowlton, C. M. Eakin, R. Iglesias-Prieto, N. Muthiga, R. H. Bradbury, A. Dubi, M. E. Hatziolos. 2007. “Coral Reefs Under Rapid Climate Change and Ocean Acidification.” *Science* 318. no. 5857: 1737-1742.

¹⁰⁴ Kleypas et al. 2006. p. 26.

¹⁰⁵ Collins, S. and G. Bell. 2004. “Phenotypic consequences of 1000 generations of selection at elevated CO₂ in a green alga.” *Nature* 431, 566–569, as cited in The Royal Society, 2005.

organisms,” several of the species studied “show increased rates of photosynthesis as CO₂ is increased above the present atmospheric level.”¹⁰⁶ They also report on laboratory experiments on a red seaweed species in which growth increased “very significantly” when exposed to CO₂ at twice the current atmospheric concentration.¹⁰⁷

On the other hand, ongoing, unpublished research on bull kelp (*Nereocystis luetkeana*) and winged kelp (*Alaria marginata*) indicate that the reproductive filaments of these species grow “noticeably slower” in lower pH seawater.¹⁰⁸ Such results raise the possibility of an important adverse effect on Sanctuary kelp species.

The coccolithophore¹⁰⁹ species *Emiliana huxleyi*, a single-celled, phytoplanktonic calcifier that exists throughout the world’s non-polar oceans, has been observed to be adversely affected by elevated atmospheric CO₂ conditions¹¹⁰, but in one case demonstrated an increase in primary production and calcification in response to such change.¹¹¹ Some other types of phytoplankton are limited by the lack of dissolved CO₂ in water, so an increase in CO₂ levels could allow these species to flourish.¹¹² Again the lack of extensive “real world” data (gathered outside the laboratory) prevents high-certainty predictions of how such species will react to higher carbon dioxide concentration ([CO₂]) in the complex, open ocean environment.

In summary, evidence suggests that rising atmospheric CO₂ levels could affect many organisms by reducing calcification, increasing dissolution of shells, causing hypercapnia, and reducing growth, reproduction and survival rates. In others, it could encourage photosynthesis and growth. Uncertainty about the impacts on photosynthesis and the possibility that some organisms might thrive in, or at least successfully adapt to, changing conditions makes predictions about species survival and ecosystemic change difficult, but strongly suggests the possibility of significant changes. The following section discusses several groups of species that appear likely to be adversely affected by ocean acidification.

b: Examples of potentially impacted organisms

Calcifying organisms can be divided into two main groups: benthic and planktonic. Major benthic, or bottom-dwelling, organisms include corals, calcifying macroalgae, benthic

¹⁰⁶ The Royal Society 2005. p. 19.

¹⁰⁷ The Royal Society 2005, citing: Kübler J.E., A.M. Johnston, and J.A. Raven. 1999. “The effects of reduced and elevated CO₂ and O₂ on the weed *Lomentaria articulata*.” *Plant Cell and Environment* 22: 1303–1310.

¹⁰⁸ Kelp research in progress by Dr. Terrie Klinger, University of Washington. As reported by Susan Milius, 2008. “The next ocean: Humanity’s extra CO₂ could brew a new kind of sea.” *Science News*, Vol. 173#11. Available at: <http://www.sciencenews.org/view/feature/id/9479> (viewed July 1, 2008).

¹⁰⁹ According to one general overview: “Coccolithophores (also called coccolithophorids) are single-celled algae, protists and phytoplankton belonging to the division haptophytes. They are distinguished by special calcium carbonate plates (or scales) of uncertain function called coccoliths. Coccolithophores are almost exclusively marine and are found in large numbers throughout the surface euphotic zone of the ocean.” “Coccolithophore.” Wikipedia. Available at <http://en.wikipedia.org/wiki/Coccolithophores> (viewed July 1, 2008).

¹¹⁰ Riebesell, U., I. Zondervan, B. Rost, P.D. Tortell, R.E. Zeebe, and F.M. Morel. 2000. “Reduced calcification of marine phytoplankton in response to increased atmospheric CO₂.” *Nature* 407: 364-7.

¹¹¹ Iglesias-Rodriguez, D.M., et al. 2008. “Phytoplankton Calcification in a High-CO₂ World.” *Science* 320 no. 5874: 336-340. doi: 10.1126/science.1154122.

¹¹² Doney 2006.

foraminifera, mollusks, gastropods, and echinoderms (like urchins and sea stars).¹¹³ Benthic organisms often play important roles in ecosystems by creating habitats for other species and reducing wave power.¹¹⁴

Planktonic calcifiers include both flora and fauna. For example, photosynthetic, single-celled *coccolithophore* species are distributed throughout the euphotic zone of the world's oceans (primarily in high latitude seas), and help provide a basis for marine foodwebs, especially in areas of low nutrients.¹¹⁵ Two key groups of calcifying fauna include the single-celled protist group *foraminifera*, numerous species of which secrete calcite into shells, and euthecosomatous pteropods, swimming snails that form aragonite shells.¹¹⁶ Foraminiferans and pteropods, which are abundant in high latitude ocean regions, are ecologically important in marine foodwebs; for example pteropods are an important food source for salmon in the Pacific Northwest.¹¹⁷ In addition, both groups play important roles in the global carbon cycle, transporting geologically significant quantities of carbon and calcium carbonate to the deep sea benthos.¹¹⁸

Below, a few key taxa of both benthic and planktonic calcifying organisms are identified, and how they could be affected by ocean acidification is examined. In addition, [Appendix 2](#) includes a table compiled by Fabry et al. (2008) cataloging prominent research and findings to date on ocean acidification effects on certain marine fauna.

Urchins and Other Echinoderms

Red and purple sea urchins are ecologically and socioeconomically important species in the CINMS. Researchers have already identified urchins as potentially being “particularly vulnerable” to ocean acidification, in part because the embryonic lifestage of these species builds the hard parts of its body (the “spicules”) using an amorphous (non-crystalline; see descriptions of the various CaCO₃ forms on pages 8 and 9), highly soluble form of calcium carbonate before transitioning to crystalline CaCO₃ as it matures.¹¹⁹ Researchers that exposed larvae of two species of urchins (*Hemicentrotus pulcherrimum* and *Echinodetra mathaei*) to increasing ambient carbon dioxide reported that “fertilization success, developmental rates, and larval size all decreased with increasing CO₂ concentration... Abnormal skeletalgenesis of the highly soluble high-magnesium CaCO₃ spicules in urchin larvae was also observed.”¹²⁰

These findings are reinforced by other data. A research team lead by Gretchen Hofmann at UC Santa Barbara is conducting physiological research on purple urchin larvae subjected to sea water at pH levels expected by 2100 based on two different IPCC scenarios. According to Hofmann, the larvae grow “short and stumpy” skeletons, and are extremely

¹¹³ Kleypas et al 2006; The Royal Society 2005.

¹¹⁴ The Royal Society 2005.

¹¹⁵ “What is a coccolithophore?” NASA Earth Observatory Reference. Responsible NASA Official: Lorraine A. Remer. Available at: <http://earthobservatory.nasa.gov/Library/Coccolithophores/printall.php> (viewed July 11, 2008).

¹¹⁶ Kleypas et al 2006.

¹¹⁷ Fabry et al. 2008.

¹¹⁸ *Id.*, p. 426.

¹¹⁹ Fabry et al. 2008.

¹²⁰ Research by: Kurihara, H., and Y. Shirayama. 2004. “Effects of increased atmospheric CO₂ on sea urchin early development.” *Marine Ecological Progress Series*, 274: 161–169. Reported in Fabry et al. 2008.

susceptible to mortality from ambient temperature change.¹²¹ Another team investigated how urchin larvae and gametes would be affected by pH levels corresponding to the year 2100 in upper-level CO₂ emissions scenarios; they found “significant reductions in sperm swimming speed and percent sperm motility,” and related reductions in fertilization success.¹²² The team concluded that their findings have “important implications for the reproductive and population viability of broadcast spawning marine species in the future acidified ocean.”¹²³

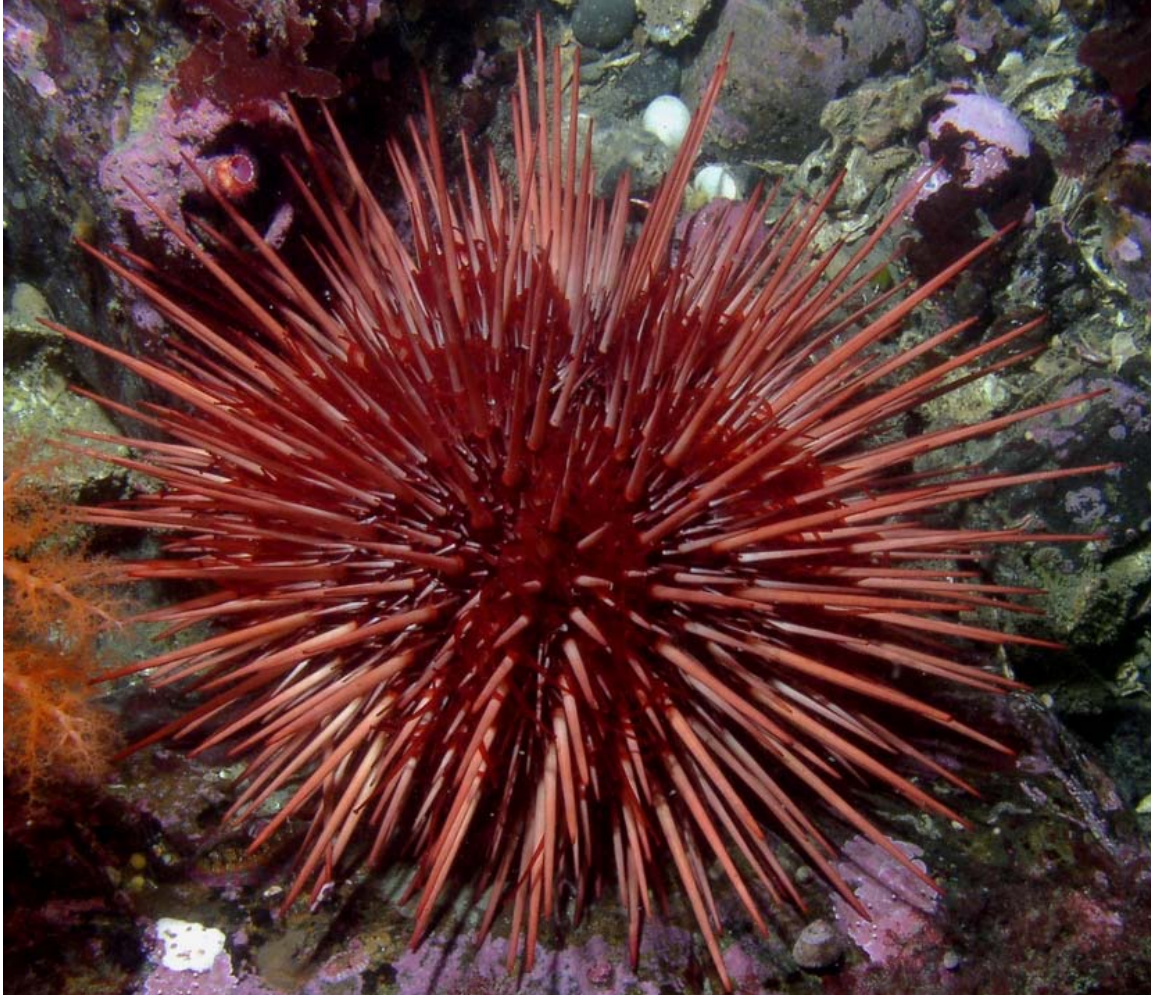


Figure 3: Red sea urchin (*Strongylocentrotus franciscanus*), an ecologically and socioeconomically important calcifier of the Northern Channel Islands (photo: Kirt L. Onthank).

However, it is important to note that physiological impacts documented by the Hofmann team and others do not necessarily inform how populations or biological communities may change in the Channel Islands region in response to decreasing pH; so little is known about the character of local physical changes that we can only speculate on resulting changes to populations and communities. Nonetheless, the strong adverse effects to

¹²¹ Kintisch, E. and E. Stokstad. “Ocean CO₂ Studies Look Beyond Coral.” News article, 22 February 2008. *Science* 319:1029, reporting on unpublished data from the Hofmann Lab, University of California, Santa Barbara.

¹²² Havenhand, J.N., F. Buttler, M.C. Thorndyke, and J.E. Williamson. 2008. “Near-future levels of ocean acidification reduce fertilization success in a sea urchin.” *Current Biology* 18: 651-652.

¹²³ *Id.*

these important species from acidified seawater that has been documented, combined with the strong degree of certainty that the ocean is and will continue to become more acidic even in the very best future emissions scenarios, should raise concerns among CINMS resource managers, its stakeholders, and the public that the issue warrants focused attention.

Abalone

These mollusks are benthic gastropods of significant regional socioeconomic importance. Several species inhabit CINMS, including the federally endangered white abalone, and the black abalone, which has been proposed by NOAA for endangered-status listing. During the 20th century, abalone species were socioeconomically important to the Channel Islands region as a recreational and commercial fishery.¹²⁴ Fabry et al. (2008) report that abalone larvae, like urchins, “may be particularly vulnerable to ocean acidification” because they too undergo a transition from highly soluble, non-crystalline calcium carbonate to standard CaCO₃ shells during embryonic development.¹²⁵ Consequently, ocean acidification could become an important factor in the continued persistence and the recovery of abalone species in and around CINMS.

The Hofmann Laboratory at UCSB is also conducting research on how red abalone (*Haliotis rufescens*) larvae, another species that range within the Channel Islands region, are affected by exposure to seawater that interfaces with the various atmospheric CO₂ levels predicted by the IPCC (2007).¹²⁶ Like the published urchin research discussed earlier, the Hofmann Lab abalone research represents an artificial scenario that will not by itself provide a basis upon which to forecast how Sanctuary red abalone and the communities of which they are a part will be affected as the ocean becomes more acidic.

Nonetheless, the data from the research will likely serve as a key component in the important task of developing an understanding of the local effects from those dynamics. Accordingly, the research and the data warrant close attention and support from CINMS staff and stakeholders.

Crustaceans

Crustaceans, such as lobster and crab, are another taxon that require calcium carbonate to form and strengthen their skeleton, and that are ecologically and socioeconomically significant to CINMS. However, no known research has been completed examining the effects of ocean acidification on either the biological calcification or the regulation of internal pH in crustacean species.¹²⁷

Corals

Corals are colonial benthic cnidarians that feed by filtering plankton out of the water.¹²⁸ What is often perceived as a single “coral” is actually a colony of thousands of genetically identical coral polyps (similar to jellies, which are also in phylum Cnidaria).

¹²⁴ Bland, Alistair. “Diving for Delicacies and Dollars: The Celebrated Past, Stagnant Present, and Possible Future of San Miguel Island’s Abalone.” *Santa Barbara Independent*. June 26, 2008. Available at: <http://independent.com/news/2008/jun/26/celebrated-past-stagnant-present-and-possible-futu/> (viewed July 1, 2008).

¹²⁵ Fabry et al. 2008.

¹²⁶ “Impacts of ocean acidification on Abalone larvae.” Hoffman Lab website. Available at: http://hofmannlab.msi.ucsb.edu/abalone_research.html (viewed July 2, 2008).

¹²⁷ Fabry et al. 2008.

¹²⁸ Kleypas et al 2006; Doney 2006.

Each polyp produces a calcium carbonate shell, which yields a colonial skeleton over thousands of polyp generations.¹²⁹ In turn, groups of corals can accumulate to form ecologically vital coral reefs within “warm, clear shallow waters of tropical oceans worldwide.”¹³⁰

Located beyond the tropics, CINMS is not known to feature coral reefs. However, it is within the range of certain solitary coral species such as orange cup coral (*Balanophyllia elegans*), which form on rocky outcroppings from British Columbia to Baja California.¹³¹ Corals have been relatively well studied with respect to both ecosystem function and how they are impacted by ocean acidification. As a result, corals exemplify how the reduction of biological calcification could cause further, potentially significant effects to non-calcifying species and marine biological communities.



Figure 4: Orange cup coral (*Balanophyllia elegans*) (photo: [Tewy](#)).

Low-latitude corals secrete aragonitic shells, while cold-water corals in the North Atlantic produce calcitic shells.¹³² These cold-water corals also create important fish habitats.¹³³ Current stresses on coral reefs include pollution, overfishing, habitat destruction,

¹²⁹ Doney 2006.

¹³⁰ “An Introduction to Coral Reefs.” Online reference, Coral Reef Ecology Home Page, University of the Virgin Islands. Available at http://manta.uvi.edu/coral_reefer/ (Viewed September 12, 2008).

¹³¹ “Orange cup coral (*Balanophyllia elegans*).” Monterey Bay Aquarium Online Field Guide. Available at http://www.mbayaq.org/efc/living_species/print.asp?inhab=152. (Viewed July 5, 2008).

¹³² Orr et al 2005.

¹³³ Doney 2006.

and climate change, which collectively are known to result in bleaching events (when symbiotic algae leave the coral cells, concluding with coral death).¹³⁴ Such events occur in high water temperatures, and possibly as a result of acidification; Doney (2006) suggests that acidification, on top of the other adverse anthropogenic factors, could push corals to a “tipping point” that results in the extinction of coral reefs and a transformation of the communities that are supported by living coral reefs.¹³⁵

Low-latitude aragonitic corals are thought to be affected most immediately by changes in ocean pH and carbonate saturation. Hoegh-Guldberg et al. (2007) report, “Many experimental studies have shown that a doubling of pre-industrial [CO₂]_{atm} to 560 ppm decreases coral calcification and growth by up to 40% through the inhibition of aragonite formation... as carbonate-ion concentrations decrease.”¹³⁶ But cold-water corals will also suffer from decreasing calcification rates.¹³⁷ In fact, the average response of corals to a doubling of the atmospheric CO₂ levels is a 30% decline in calcification. Dissolution of existing coral shells is likely to increase simultaneously.¹³⁸

Coralline algae

Coralline algae are abundant and widespread autotrophic organisms that form on rocky outcroppings around the world, and are often important members of benthic systems.¹³⁹ They form high-Mg calcite “shells”, and contribute to the calcification of many reefs.¹⁴⁰ Like corals, research suggests that this taxon is likely to suffer reduced calcification and increased dissolution as a result of ocean acidification. For example, Kuffner et al. (2007) investigated how crustose coralline algae, a cosmopolitan species, was affected in laboratory-simulated environments (“mesocosms”) featuring elevated CO₂ levels. They found that “the recruitment rate and growth of crustose coralline algae were severely inhibited in the elevated carbon dioxide mesocosms,” and consequently went on to conclude that “ocean acidification due to human activities could cause significant change to benthic community structure in shallow-warm-water carbonate ecosystems.”¹⁴¹

The Kuffner et al. results are of particular relevance to CINMS, because the presence of crustose coralline algae on rocky outcroppings is known to enhance the settlement and recruitment of invertebrate grazing organisms, particularly abalone species.¹⁴² Consequently, the impingement of calcification and growth of coralline algae as a result of ocean acidification could represent an additional ocean acidification-caused stressor for regional abalone populations, several of which are of particular management and/or socioeconomic concern.

Foraminifera

¹³⁴ *Id.*

¹³⁵ *Id.*

¹³⁶ Hoegh-Guldberg et al., 2007.

¹³⁷ Orr et al 2006.

¹³⁸ Kleypas et al 2006.

¹³⁹ *Id.*

¹⁴⁰ Doney 2006.

¹⁴¹ Kuffner, I.B., A.J. Andersson, P.L. Jokie, K.S. Rodgers, and F.T. Mackenzie. 2007. “Decreased abundance of crustose coralline algae due to ocean acidification.” *Nature Geoscience* 1: 114-117. doi:10.1038/ngeo100.

¹⁴² Boxshall, A.J. 2000. “The importance of flow and settlement cues to larvae of the abalone, *Haliotis rufescens*.” *Journal of Experimental Marine Biology and Ecology*. Vol.254, Issue 2: 143-167.

Phylum Foraminifera, in the kingdom Protista, comprises a large group of single-celled, amoeba-like organisms that make shells known as “tests” and harvest food with a mesh of fine strands of tissue¹⁴³ According to Fabry et al. (2008), foraminiferans “are widely distributed in the upper ocean,” and, along with coccolithophores, “are thought to produce the majority of pelagic CaCO₃.”¹⁴⁴ Foraminiferans are also known to be important to marine trophic systems, as they can represent an extremely abundant food source for larger predators such as snails, echinoderms, and fish, some of which “are very selective about which [foraminiferan] species they eat.”¹⁴⁵

There are both benthic and planktonic species of foraminifera. The planktonic forms are surface-dwelling, calcitic, heterotrophic (consumer) plankton.¹⁴⁶ All foraminifera form high-Magnesium calcite CaCO₃ during the initial stages of calcification.¹⁴⁷ During this process, the organism captures water and increases its pH to a certain point. If the initial pH of the water is reduced due to acidification, the organism must use more energy in order to raise the pH to that same point.¹⁴⁸ According to the Royal Society’s review of literature, foraminiferan species *Orbulina universa*, *Globigerinoides sacculifer*, *Amphistegina lobifera* and *A. hemprichii* all were documented to experience shell weight reduction in proportion to lower [CO₃²⁻] in their environment.¹⁴⁹ On the other hand, Fabry et al. (2008) report that “temperature and food supply also strongly affect foraminiferal calcification,” and thus “future increases in sea surface temperatures could lead to higher foraminiferal growth rates.”¹⁵⁰

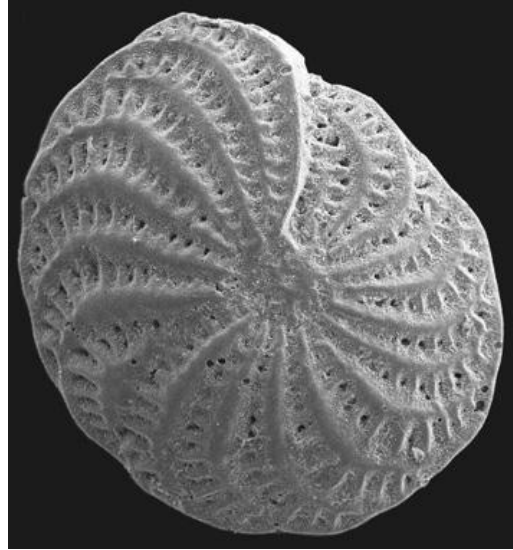


Figure 5: Example foraminifera test. Width approx. 750µm (photo: Univ. of Tasmania).

Pteropods

Pteropods are small planktonic, swimming snails within the phylum Mollusca, and the order Opisthobranchia. Pteropod species are found in the Southern, Arctic, and Sub-Arctic Pacific oceans, and are the dominant zooplankton in the Ross Sea.¹⁵¹ Pteropods represent an important food source for an array of other animals in regions where they are abundant, including fish, whales, and other mollusks. For example, researchers have reported that pteropod population declines can cause declines in the populations of other

¹⁴³ Hemleben, C., M. Spindler, and O.R. Anderson. 1989. *Modern Planktonic Foraminifera*. Springer-Verlag, Berlin, Germany. 363 pgs. As cited in “Foraminifera.” Wikipedia (English). Available at <http://en.wikipedia.org/wiki/Foraminifera> (viewed July 2, 2008).

¹⁴⁴ Fabry et al. 2008.P.417, citing Schiebel 2002.

¹⁴⁵ Wetmore. K.L. Wetmore. 1995. “Foraminifera: Life History and Ecology.” University of California Museum of Paleontology. Available at: <http://www.ucmp.berkeley.edu/foram/foramlh.html> (viewed July 11, 2008).

¹⁴⁶ Orr et al 2005; Kleypas et al 2006.

¹⁴⁷ The Royal Society 2005.

¹⁴⁸ *Id.*

¹⁴⁹ *Id.*, citing Bijma et al. 1999 and 2002, and Erez 2003.

¹⁵⁰ Fabry et al. 2008, citing Barker and Elderfield 2002, and Bijma et al. 2002.

¹⁵¹ Orr et al 2005.

predatory pteropods¹⁵², and in the biomass of pink salmon in the North Pacific¹⁵³. Shelled pteropods are major planktonic producers of aragonite shells.¹⁵⁴

As described above, ocean acidification is causing high-latitude regions to become undersaturated with respect to aragonite. Data from laboratory testing of one species of pteropod (of which there are approximately 50), suggest that the group reduces its calcification rate in response to ocean acidification.¹⁵⁵ However, Fabry et al. note with caution that “Species-specific responses are likely,” and the lack of testing of other members of the group “precludes the identification of general trends.” Nonetheless, there is evidence that, in seawater that becomes undersaturated with respect to aragonite, pteropods may not be able to maintain their shells, and will be forced to shift their habitat to lower latitudes. Unfortunately, it is unclear whether or not they will survive this transition to warmer waters.¹⁵⁶

IV. Ecosystem Effects

a: Overview

Experts in physical and biological oceanography studying ocean acidification are just beginning to identify general patterns in how marine ecology will be affected by ocean acidification. Below are a few excerpts from recent prominent studies of ocean acidification, including those relied upon elsewhere in this report.

Guinotte et al. (2006):

Many species of plankton (eg coccolithophores and foraminiferans) and pteropods (small gastropod mollusks), which form the base of marine food webs, use carbonate ions to build their CaCO₃ shells/tests and are sensitive to the seawater chemistry changes previously noted (Riebesell *et al.* 2000; Riebesell 2004; Orr *et al.* 2005). If changing seawater chemistry causes a reduction in phytoplankton and zooplankton production in surface waters, the feedback to deep-sea coral ecosystems will probably be negative, as deep-sea corals may not be able to attain their nutritional requirements.... The oceans are changing both chemically and physically as a result of the uptake of anthropogenic CO₂. Shallow-water corals and other marine calcifiers react negatively when exposed to reduced carbonate saturation state conditions. Biological feedbacks and the reactions of marine organisms to these changes will be complex and will probably affect all trophic levels of the world's oceans.

Fabry et al. (2008):

Although the changes in seawater chemistry that result from the oceanic uptake of anthropogenic CO₂ are well characterized over most of the ocean, the biological impacts of ocean acidification on marine fauna are only beginning to be understood. Nevertheless, sufficient information exists to state with certainty that deleterious impacts on some marine species are unavoidable, and that substantial alteration of marine ecosystems is likely over the next century.... We conclude that ocean

¹⁵² Seibel, B. A., and H.M. Dierssen. 2003. "Cascading trophic impacts of reduced biomass in the Ross Sea, Antarctica: Just the tip of the iceberg?" *The Biological Bulletin*. Vol. 205, pgs. 93-97.

¹⁵³ Fabry et al., 2008, p. 426.

¹⁵⁴ Orr et al 2005, Kleypas et al 2006.

¹⁵⁵ Fabry et al. 2008.

¹⁵⁶ Orr et al 2005.

acidification and the synergistic impacts of other anthropogenic stressors provide great potential for widespread changes to marine ecosystems.

Feely et al. (2008):

Water already in transit to upwelling centers is carrying increasing anthropogenic CO₂ 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 CO₂. 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... This phenomenon... 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.

In a study published in July of 2008, Hall-Spencer et al. explored the question of how ocean acidification actually affects coastal, benthic ecosystems by studying marine life around subsea volcanic vents in a rocky nearshore area. The volcanic discharge into the water column was rich in CO₂, and caused a local gradient in seawater pH that ranged from a minimum of 7.4 to “normal” at 8.1-8.2. The researchers found that:

Sea-grass production was highest in an area at mean pH 7.6... where coralline algal biomass was significantly reduced and gastropod shells were dissolving due to periods of carbonate sub-saturation. The species populating the vent sites comprise a suite of organisms that are resilient to naturally high concentrations of pCO₂ and indicate that ocean acidification may benefit highly invasive non-native algal species.¹⁵⁷

Their findings may seem somewhat unsurprising given the similar conclusions reported in the biological studies reviewed in the previous section. However, as Hall-Spencer et al. point out, most if not all of those studies were on single, isolated species isolated in a laboratory environment:

...our results provide the first *in situ* insights into how shallow water marine communities might change when susceptible organisms are removed owing to ocean acidification...

...to our knowledge, this is the first ecosystem-scale validation of predictions that these important groups of organisms are susceptible to elevated amounts of p CO₂.¹⁵⁸

b: Changes in and around CINMS

The high level of certainty associated with predicted changes to the ocean's chemical qualities due to rising atmospheric [CO₂], as well as some emerging data, suggest that broad-scale biological oceanographic changes are also likely to occur due to ocean acidification. However, despite a strong indication that ecosystem changes will occur, two important

¹⁵⁷ Hall-Spencer, J.M., R. Rodolfo-Metalpa, S. Martin, E. Ransome, M. Fine, S.M. Turner, S.J. Rowley, D. Tedesco, and M. Buia. 2008. “Volcanic carbon dioxide vents show ecosystem effects of ocean acidification.” *Nature* 454: 96-99. doi:10.1038/nature07051.

¹⁵⁸ Id.

limitations in the scientific record prevent detailed speculation with respect to *how* Channel Islands ecosystems specifically will be affected by these changes.

First, the existing data on the biological and physical dynamics related to ocean acidification is relatively patchy, i.e. based on data points distributed over ocean basin-scale areas, and a few individual calcifying species that represent large taxonomic groups.

Second, there is a distinct lack of data regarding whether or not organisms within the Sanctuary region will be able to adapt to pH and carbonate saturation changes at the rate such changes actually occur in the years and decades ahead. For example, while the Hofmann Lab's studies on larval urchin and abalone demonstrate how individual animals respond to various low-pH environments, it remains unknown how the various populations of calcifying species that comprise Sanctuary ecosystems will be affected over the course of multiple generations, as regional pH begins to change and move toward the Hofmann Lab's scenarios. Will all calcifying organisms die off and be replaced by certain seaweeds, or will some species be able to adapt in time, and persist? Which species will be most affected, and when, and will their roles within the ecosystem be able to be filled by other organisms?

The present lack of understanding of the temporal component to local ecosystem change due to ocean acidification is perhaps the greatest challenge to preparing Sanctuary resource managers to address the issue. However, it thus also represents a clear starting point for resource managers and Sanctuary stakeholders in that preparation.

The underlying chemistry of ocean acidification, as a phenomenon that will affect the pH and the carbonate saturation state of most of the world ocean in the years and decades ahead, appears to be understood with a very high degree of certainty among the oceanographic science community. Furthermore, while prominent ocean-scale modeling projects significant changes on a time scale of decades, evidence from the field indicates that significant changes to pH and carbonate concentration are already occurring off California on a local basis. This confluence of dynamics— an apparent inevitability of pH change and the risk of profound ecosystem effects, combined with significant uncertainty of the temporal scale of the change— is central to the articulation of potential management responses from CINMS staff, its resource management partners, and its public stakeholders.

V. Recommendations for CINMS

Coastal regions, which can be greatly impacted by anthropogenic-driven ocean acidification, are not well-represented in global ocean–atmosphere coupled models, because of lack of data, complexities of nearshore circulation processes, and too-coarse model resolution. Given the importance of coastal areas to fisheries and other marine resources and services, coastal ecosystems constitute a target region where research is urgently needed.

- Dr. Victoria Fabry and coauthors, 2008.¹⁵⁹

Relative to the global scale of both the causes and the effects of ocean acidification, the management tools available to Sanctuary staff and its stakeholders may seem so small as to be irrelevant. Clearly, the fundamental solution to ocean acidification is a stabilization and eventual reduction of global CO₂ emissions, a daunting enough task for the international community, let alone CINMS or its Advisory Council.

Nonetheless, CINMS stakeholders and resource managers have a mandate and responsibility to protect and conserve the extraordinary resources and qualities that are harbored within Sanctuary boundaries, irrespective of the challenges confronting that mission. Ocean acidification— a problem with potentially profound consequences and an ultimately global geographic reach— is no different.

While a global CO₂ emissions reduction is the most pressing need with respect to protecting the ocean, addressing and preparing for ocean acidification will require an array of additional efforts, including research, monitoring, public education, and development of resource management strategies in the context of a rapidly changing physical oceanographic context. Such work is needed not only to help foster the will and generate the ideas needed to directly address ocean acidification, but also to provide potentially vital information for efforts to conserve the integrity of Channel Islands ecosystems in the midst of the forecasted changes.

Fortunately, CINMS is already endowed with numerous assets, institutional partnerships, and research opportunities that can be leveraged to begin fulfilling these needs.

The Commercial Fishing and Conservation Working Groups of the SAC have identified four key objectives for CINMS stakeholders and staff to adopt as a starting point for understanding and managing ocean acidification within Sanctuary boundaries— *Research, Monitor, Educate and Lead*. Within each objective, specific recommendations are presented to help achieve that goal.

1. **Research.** CINMS should prioritize the organization of a baseline of physical and biological oceanographic data relevant to understanding the local effects of ocean acidification, systematically identify data gaps and research needs, and begin forming partnerships with researchers and institutions that can illuminate those dynamics and fulfill those needs.
 - a. In order to identify research and monitoring needs, CINMS staff should identify the important physical and biological oceanographic parameters relevant to ocean

¹⁵⁹ Fabry, V. J., B.A. Seibel, R.A. Feely, and J.C. Orr. 2008. "Impacts of ocean acidification on marine fauna and ecosystem processes." *ICES Journal of Marine Science*, 65: 414–432.

acidification within the Channel Islands, and then determine whether or not these data are being collected within the Sanctuary region. Such information could help shape the scientific efforts of the Sanctuary's academic and government research partners, and provide the background necessary for coordinating needed monitoring efforts. Two important examples include:

- i. Cataloging the Sanctuary's calcifying organisms and determining which would be good candidates for long term study;
 - ii. Identifying the most important physical oceanographic parameters relative to tracking ocean acidification-related changes, and determining which (if any) of the Sanctuary's research partners are gathering data on these parameters.
- b. CINMS should compile and organize the gaps and needs it identifies among the research currently underway. This list of needs could be highly useful for coordinating the Sanctuary's overall research program, for consultation with potential new research partners, and in helping shape the strategic plans of research funding entities such as Sea Grant and the Ocean Protection Council.
- c. Numerous opportunities for useful research partnerships exist for CINMS, which it should actively pursue. In addition to providing research guidance based on the list of gaps and needs it compiles, CINMS could provide critical logistical support to facilitate academic and government scientists. CINMS should identify, and communicate with, researchers and institutions that are investigating ocean acidification and dynamics along the West Coast, to determine which potential partnerships should be pursued. Examples that emerged from the research for this report include:
- i. The aforementioned Hofmann and Fabry Laboratories— which are conducting acidification research on the physiology of multiple species of particular socioeconomic, ecological, and management interest to Sanctuary staff and stakeholders.
 - ii. NOAA's Pacific Marine Environment Lab¹⁶⁰, whose staff led the discovery of the upwelling of undersaturated sea water off the coast of northern California, and whose future efforts could illuminate these dynamics around the Channel Islands.
 - iii. Dr. Wei-Jun Cai¹⁶¹, Department of Marine Sciences at the University of Georgia, who has been compiling a record of alkalinity data in the Santa Barbara Channel region in coordination with UCSB's Department of Geography.
- d. CINMS should consult with the National Marine Sanctuary Program's West Coast Regional Director, to identify opportunities for greater research and monitoring efficiency, and additional data gathering, through coordinating of ocean acidification research and monitoring among all the West Coast Sanctuary sites.

2. **Monitor.** CINMS and its research partners should create an organizational framework to *track changes* in acidification-related physical and biological indicators over time,

¹⁶⁰ <http://www.pmel.noaa.gov/>

¹⁶¹ <http://www.marsci.uga.edu/directory/wjcai.htm>

including how the Sanctuary's calcifying species and their ecosystems are affected by changes in pH and carbonate saturation.¹⁶²

- a. Such a project would fit naturally within ongoing monitoring of other biological and water quality monitoring efforts. In addition, an ongoing data stream of this nature could help improve the understanding of nearshore ocean acidification dynamics, and help improve existing models used to understand the linkages between the atmosphere and the ocean. CINMS staff should consult with acidification scientists to determine the most important oceanographic variables to track, and whether or not existing monitoring efforts could simply be expanded to include the CINMS region.
 - b. CINMS marine reserves could help yield additional insights with respect to ecosystem resilience in the context of ocean acidification and other simultaneous stressors; such information could be of value for marine resource managers in the years to come.
- 3. Educate.** CINMS should use its existing education and outreach programs to help increase awareness of ocean acidification among Sanctuary stakeholders and the public. Content should include the causes of ocean acidification, its effects on Sanctuary resources, qualities and ecosystems, and actions that the public and stakeholders can take to reduce their contribution to ocean acidification.
- a. Existing programs like MERITO (Multicultural Education for Resource Issues Threatening Oceans¹⁶³), the Channel Islands Naturalist Corps, and the Advisory Council could serve as good vehicles for this effort.
 - b. Educational programs and products should incorporate CINMS-specific information with respect to ocean acidification as it is produced from current and future research and monitoring efforts.
- 4. Lead.** CINMS staff should seize the opportunity to address ocean acidification through leadership among local ocean users, the public, and within the National Marine Sanctuary Program and NOAA. CINMS leadership actions are needed in two areas: (a) CO₂ emissions reduction, and (b) management planning and coordination.
- a. Emissions reduction
 - i. CINMS should pursue the completion of an audit of CO₂ emissions associated with Sanctuary operations, and identify measures that can reduce, offset, and ideally eliminate such emissions toward a goal of operational carbon neutrality. The Sanctuary should work to complete this audit within one year, so that specific measures to reduce emissions can begin being included within Sanctuary budgetary planning within upcoming budget cycles. Channel Islands National Park already serves as an excellent model in

¹⁶² Fabry et al. (2008) provide a suite of important research recommendations as the conclusion to their report. In addition to the quote that leads this section, they offer additional advice with particular relevance to CINMS, stating:

In sensitive regions and for critical species, we need to track the abundances and depth distributions of calcareous and noncalcifying fauna, measure calcification and metabolic rates of these groups, and relate these data to changes in the CO₂ chemistry of the water column. This requires commitment to long-term monitoring programmes at appropriate temporal and spatial scales to detect possible shifts, and distinguish between natural variability and anthropogenically induced changes.

¹⁶³ Overview of the CINMS MERITO program available at <http://channelislands.noaa.gov/edu/merito.html>

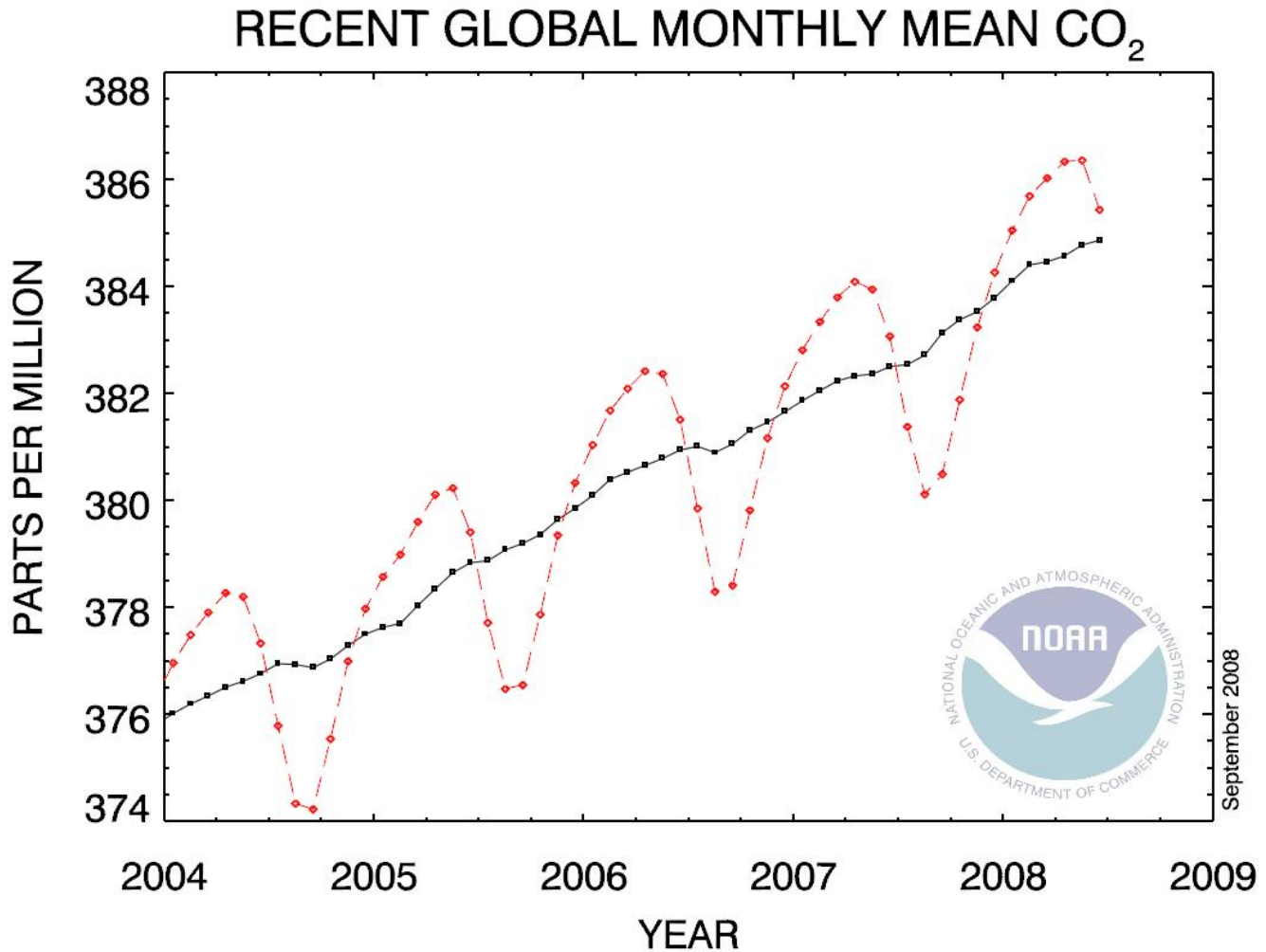
this regard through the operation of its biodiesel-fueled vessels.¹⁶⁴ CINMS staff should work to emulate this example and improve upon it, and then publicize their efforts among Sanctuary users, the general public, and the other NMSP sites.

- ii. CINMS staff should work collaboratively with its stakeholders to reduce CO₂ emissions from all activities and uses associated with the Sanctuary. This could be initiated by including CO₂ emissions inventorying and reduction measures as prominent components for the next CINMS management plan update, asking CINMS user groups to inventory and reduce their emissions in a parallel timeline to the Sanctuary's own efforts, and soliciting CINMS users for ideas on how the Sanctuary can meaningfully and efficiently contribute to reducing the carbon intensity of CINMS uses.
- b. Management Planning
- i. Include study and action plans for CO₂-related climate change effects, including ocean acidification, sea level rise, and temperature changes, in future CINMS management planning efforts. Coordinate with the West Coast Regional Director to identify any multi-site efficiencies for this planning.
 - ii. The CINMS superintendent should advocate within the National Marine Sanctuary Program for NOAA to support individual sites in improving their understanding of ocean acidification and its resource management implications.
 - iii. The CINMS superintendent should also encourage, where appropriate, the NMSP director and NOAA to set overarching policy on ocean acidification, and take actions to help individual sites to protect their resources from its adverse effects. These actions could include:
 - 1. Coordinating ocean acidification research and management efforts among NOAA's relevant departments and programs (such as NMFS, the Pacific Marine Environment Laboratory, and the NMSP).
 - 2. Providing adequate funding for CINMS and other sites to conduct local research, management and outreach and education for ocean acidification.
 - 3. Identification and research of ocean acidification impact mitigation measures. If severe changes occur in CINMS (or any other Sanctuaries), protection of Sanctuary resources and qualities may require active management efforts to counter direct, adverse impacts. For example, specific actions may be needed to bolster or replenish populations of species of particular ecological importance that become weakened or reduced by ocean acidification. The CINMS Superintendent should encourage NOAA to take responsibility for research and development of potential ocean acidification impact mitigation measures, to ensure that they are both effective and compatible with NMSP objectives and regulations.
 - 4. Investigation of opportunities to collaborate with international marine protected area agencies, e.g. through coordination of ocean acidification research, monitoring, or other management activities.

¹⁶⁴ "A Power to Preserve." *Biodiesel Magazine*, July/August 2004. Jessica Williams, Dave Nilles, and Julie Bratvold. Available at: http://www.biodieselmagazine.com/article.jsp?article_id=533 (Viewed July 5, 2008).

Appendix 1 – NOAA graphs: atmospheric CO₂ concentration and Ocean pH

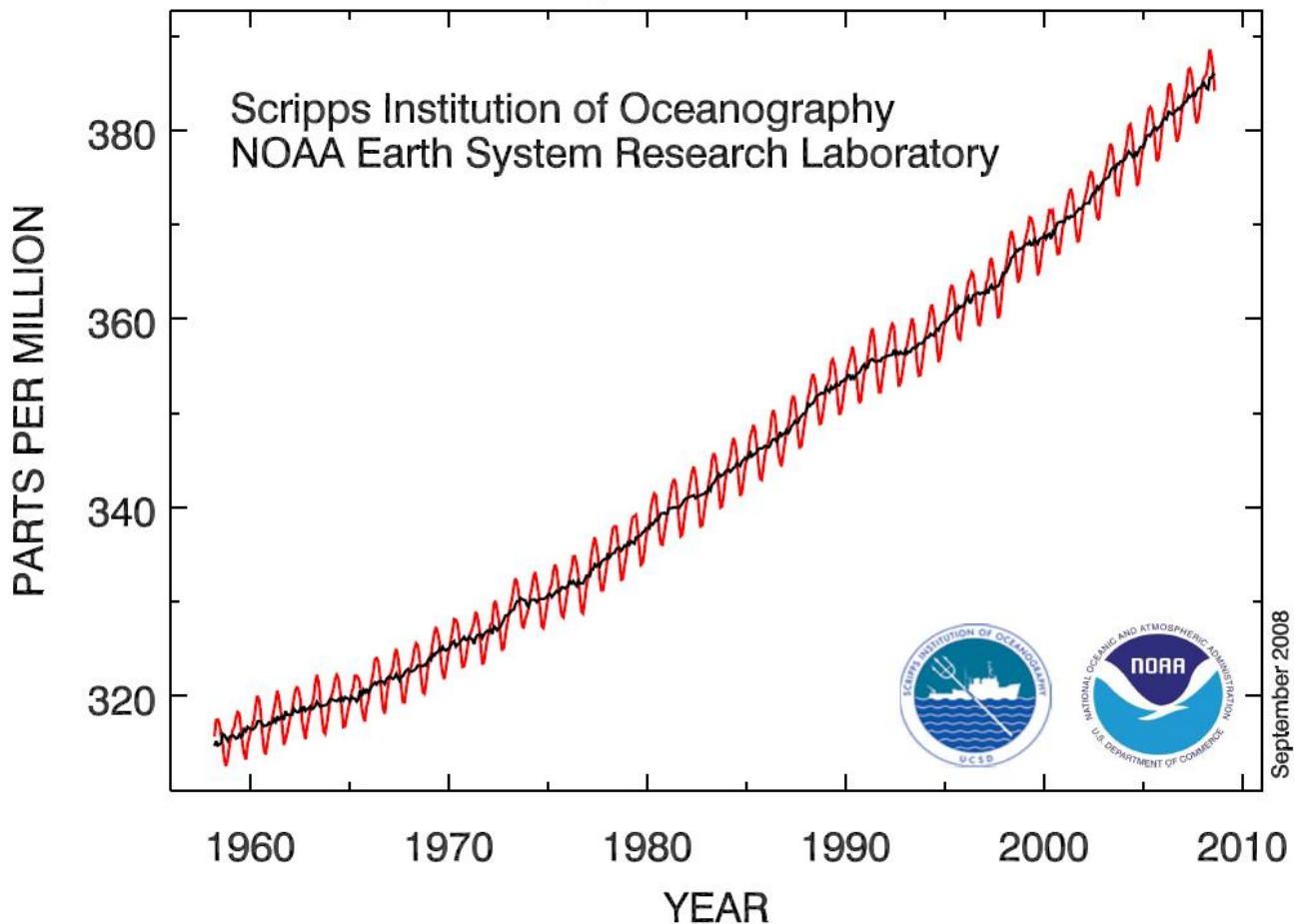
Graphs and explanatory narratives excerpted from NOAA’s Earth System Research Laboratory (ESRL), Global Monitoring Division (www.esrl.noaa.gov/gmd/cgg/trends). The red line represents monthly mean values; the black line represents the same data corrected for average seasonal cycle.



NOAA ESRL:

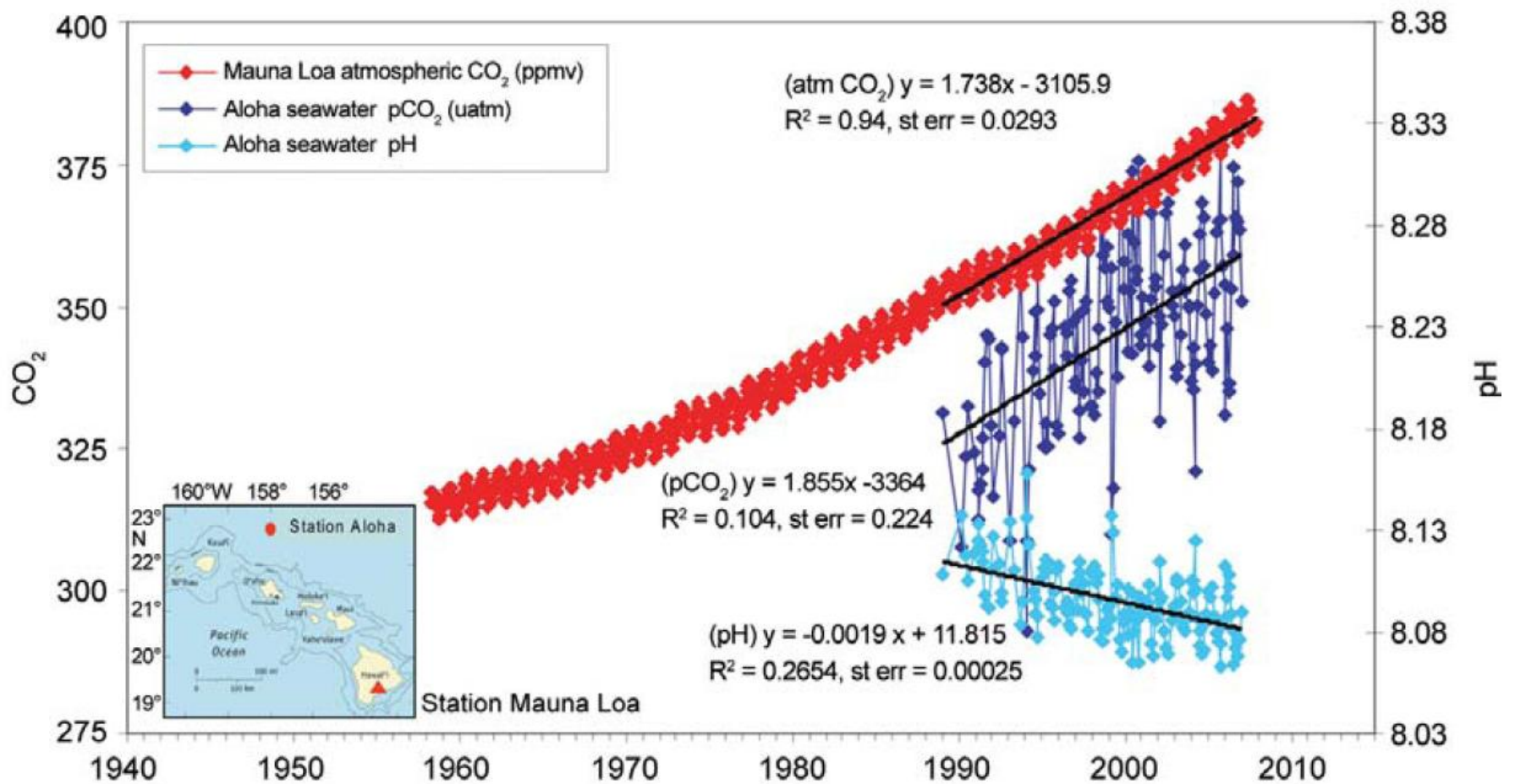
“The graph shows recent monthly mean carbon dioxide globally averaged over marine surface sites. The ESRL has measured carbon dioxide and other greenhouse gases for several decades at a globally distributed network of air sampling sites. Data are reported as a dry mole fraction defined as the number of molecules of carbon dioxide divided by the number of molecules of dry air, multiplied by one million (ppm).”

Atmospheric CO₂ at Mauna Loa Observatory



NOAA ESRL:

“Monthly mean atmospheric carbon dioxide at Mauna Loa Observatory, Hawaii. The carbon dioxide data, measured as the mole fraction in dry air, on Mauna Loa constitute the longest record of direct measurements of CO₂ in the atmosphere. They were started by C. David Keeling of the Scripps Institution of Oceanography in March of 1958 at a facility of the National Oceanic and Atmospheric Administration (Keeling, 1976). NOAA started its own CO₂ measurements in May of 1974, and they have run in parallel with those made by Scripps since then (Thoning, 1989).”



“Time series of atmospheric CO₂ at Mauna Loa (ppmv) and surface ocean pH and pCO₂ (uatm) 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, www.esrl.noaa.gov/gmd/ccgg/trends/; HOTS/Aloha data: Dr. David Karl, University of Hawaii, <http://hahana.soest.hawaii.edu/>].”

Graph and caption excerpted from: Feely, R.A. 2008. “Ocean Acidification.” In: *State of the Climate in 2007*. D. H. Levinson and J. H. Lawrimore eds. *Bulletin of the American Meteorological Society*, **89**, S58. Available at: <http://www.ncdc.noaa.gov/oa/climate/research/2007/ann/bams/>

Appendix 2

Table excerpted from Fabry et al. 2008¹⁶⁵: “Examples of the response of marine fauna to ocean acidification” [continued on following page].

Species	Description	CO ₂ system parameters	Sensitivity	Reference
Planktonic foraminifera				
<i>Orbulina universa</i>	Symbiont-bearing	pCO ₂ 560–780 ppmv	8–14% reduction in shell mass	Spero et al. (1997); Bijma et al. (1999, 2002)
<i>Globigerinoides sacculifer</i>	Symbiont-bearing	pCO ₂ 560–780 ppmv	4–8% reduction in shell mass	Bijma et al. (1999, 2002)
Cnidaria				
Scyphozoa Hydrozoa	Jellyfish	North Sea seawater pH drop from 8.3 to 8.1	Increase in frequency as measured by CPR from 1958 to 2000	Attrill et al. (2007)
Mollusca				
<i>Clio pyramidata</i>	Shelled pteropod	$\Omega_{\text{arag}} < 1$	Shell dissolution	Feely et al. (2004); Orr et al. (2005); this work Harris et al. (1999).
<i>Haliotis laevis</i>	Greenlip abalone	pH 7.78; pH 7.39	5% and 50% growth reductions	
<i>Haliotis rubra</i>	Blacklip abalone	pH 7.93; pH 7.37	5% and 50% growth reductions	
<i>Mytilus edulis</i>	Mussel	pH 7.1 / 10 000 ppmv pCO ₂ 740 ppmv	Shell dissolution 25% decrease in calcification rate	Lindinger et al. (1984) Gazeau et al. (2007)
<i>Crassostrea gigas</i>	Oyster	pCO ₂ 740 ppmv	10% decrease in calcification rate	
<i>Mytilus galloprovincialis</i>	Mediterranean mussel	pH 7.3, ~5000 ppmv	Reduced metabolism, growth rate	Michaelidis et al. (2005)
<i>Placopecten magellanicus</i>	Giant scallop	pH < 8.0	Decrease in fertilization and embryo development	Desrosiers et al. (1996)
<i>Tivela stultorum</i>	Pismo clam	pH < 8.5	Decrease in fertilization rates	Alvarado-Alvarez et al. (1996)
<i>Pinctada fucada</i>	Japanese pearl oyster	pH 7.7	Shell dissolution, reduced growth	Reviewed in Knutzen (1981)
<i>Pinna martensii</i>	Oyster	pH > 7.4	Increasing mortality	
<i>Mercenaria mercenaria</i>	Clam	$\Omega_{\text{arag}} = 0.3$	Juvenile shell dissolution leading to increased mortality	Green et al. (2004)
<i>Illex illecebrosus</i>	Epipelagic squid	2000 ppmv	Impaired oxygen transport	Pörtner and Reipschläger (1996)
<i>Dosidicus gigas</i>	Epipelagic squid	0.1% CO ₂ , ~1000 ppmv	Reduced metabolism/scope for activity	Rosa and Seibel (unpublished)
Arthropoda				
<i>Acartia steueri</i>	Copepod	0.2–1%CO ₂	Decrease in egg hatching success;	Kurihara et al. (2004)
<i>Acartia erythraea</i>	Copepod	~2000–10 000 ppmv	increase in nauplius mortality rate	
Copepods	Pacific, deep vs. shallow	860–22 000 ppmv CO ₂	Increasing mortality with increasing CO ₂ concentration and duration of exposure	Watanabe et al. (2006)
<i>Euphausia pacifica</i>	Krill	pH < 7.6	Mortality increased with increasing exposure time and decreasing pH	Yamada and Ikeda (1999)
<i>Paraeuchaeta elongata</i>	Mesopelagic copepod			
<i>Conchoecia</i> sp.	Ostracod			
<i>Cancer pagurus</i>	Crab	1% CO ₂ , ~10 000 ppmv	Reduced thermal tolerance, aerobic scope	Metzger et al. (2007)
Chaetognatha				
<i>Sagitta elegans</i>	Chaetognath	pH < 7.6	Mortality increased with increasing exposure time and decreasing pH	Yamada and Ikeda (1999)
Echinodermata				
<i>Strongylocentrotus purpuratus</i>	Sea urchin	pH ~6.2–7.3	High sensitivity inferred from lack of pH regulation and passive buffering via test dissolution during emersion	cf. Burnett et al. (2002)
<i>Psammechinus miliaris</i>	Sea urchin			Spicer (1995); Miles et al. (2007)
<i>Hemicentrotus pulcherrimus</i>	Sea urchin	~500–10 000 ppmv	Decreased fertilization rates, impacts larval development	Kurihara and Shirayama (2004)
<i>Echinometra mathaei</i>	Sea urchin			
<i>Cystechinus</i> sp.	Deep-sea urchin	pH 7.8	80% mortality under simulated CO ₂ sequestration	Barry et al. (2002)

¹⁶⁵ Fabry, V. J., B.A. Seibel, R.A. Feely, and J.C. Orr. 2008. “Impacts of ocean acidification on marine fauna and ecosystem processes.” *ICES Journal of Marine Science*, 65: 423–4.

Fabry et al. (2008) [continued from previous page].

Species	Description	CO ₂ system parameters	Sensitivity	Reference
Sipuncula				
<i>Sipunculus nudus</i>	Peanut worm	1% CO ₂ , 10 000 ppmv	Metabolic suppression Pronounced mortality in 7-week exposure	Pörtner and Reipschläger (1996) Langenbuch and Pörtner (2004)
Vertebrata				
<i>Scyliorhinus canicula</i>	Dogfish	pH 7.7 / 0.13%CO ₂ 7% CO ₂ , ~70 000 ppmv	Increased ventilation 100% mortality after 72 h	Reviewed in Truchot (1987) Hayashi <i>et al.</i> (2004)
<i>Sillago japonica</i>	Japanese whiting	7% CO ₂ , ~70 000 ppmv	Rapid mortality in 1-step exposure	Kikkawa <i>et al.</i> (2006)
<i>Paralichthys olivaceus</i>	Japanese flounder	5% CO ₂ , ~50 000 ppmv	100% mortality within 48 h	Hayashi <i>et al.</i> (2004)
<i>Euthynnus affinis</i>	Eastern little tuna	15%CO ₂ , ~150 000 ppmv	100% mortality of eggs after 24 h	Kikkawa <i>et al.</i> (2003)
<i>Pagrus major</i>	Red sea bream	5%CO ₂ , ~50 000 ppmv	>60% larval mortality after 24 h	Ishimatsu <i>et al.</i> (2005)
<i>Seriola quinqueradiata</i>	Yellowtail/ amberjack	5% CO ₂ , 50 000 ppmv	Reduced cardiac output; 100% mortality after 8 h	Ishimatsu <i>et al.</i> (2004)
<i>Sparus aurata</i>	Mediterranean fish	pH 7.3, ~ 5000 ppmv	Reduced metabolic capacity	Michaelidis <i>et al.</i> (2007)
<i>Dicentrarchus labrax</i>	Sea bass	pH 7.25, 24 mg l ⁻¹ CO ₂	Reduced feed intake	Cecchini <i>et al.</i> (2001)

Works Cited

- 45 Fed. Reg. 65198, October 2, 1980.
- 72 Fed. Reg. 29214, May 24, 2007.
- Atkins, P. and L. Jones. 1999. *Chemical Principles: The Quest for Insight*. W.H. Freeman and Company, New York. 908 pgs.
- Baird, C. and M. Cann. *Environmental Chemistry, Third Edition*. Colin Baird and Michael Cann, W.H. Freeman and Company, New York, 2005.
- Bland, Alistair. "Diving for Delicacies and Dollars: The Celebrated Past, Stagnant Present, and Possible Future of San Miguel Island's Abalone." *Santa Barbara Independent*. June 26, 2008. Available at: <http://independent.com/news/2008/jun/26/celebrated-past-stagnant-present-and-possible-futu/> (viewed July 1, 2008).
- Boxshall, A.J. 2000. "The importance of flow and settlement cues to larvae of the abalone, *Haliotis rufescens*." *Journal of Experimental Marine Biology and Ecology*. Vol.254, Issue 2: 143-167.
- Caldeira, K., and M. E. Wickett. 2005. Ocean model predictions of chemistry changes from carbon dioxide emissions to the atmosphere and ocean. *J. Geophysical Research*, 110, C09S04, doi:10.1029/2004JC002671.
- Caldeira, K., and M.E. Wickett. 2003. "Anthropogenic carbon and ocean pH." *Nature* 425:365.
- Cao, L., K. Caldeira, and A. K. Jain. 2007. "Effects of carbon dioxide and climate change on ocean acidification and carbonate mineral saturation." *Geophysical Research Letters*, 34, L05607, doi:10.1029/2006GL028605.
- Carnegie Institution for Science. "CO₂ emissions could violate EPA ocean-quality standards within decades." Press Release, September 29, 2007.
- CINMS Sanctuary Advisory Council 2008 Work Plan. Adopted March 14, 2008. Available at <http://channelislands.noaa.gov/sac/pdf/2008WPF.pdf> (viewed May 1, 2008).
- Collins, S. and G. Bell. 2004. "Phenotypic consequences of 1000 generations of selection at elevated CO₂ in a green alga." *Nature* 431: 566–569.
- Division of Atmospheric Research, CSIRO, Aspendale, Victoria, Australia, Laboratoire de Glaciologie et Géophysique de l'Environnement, Saint Martin d'Heres-Cedex, France, and Antarctic CRC and Australian Antarctic Division, Hobart, Tasmania, Australia. June 1998. "Historical CO₂ record derived from a spline fit (20 year cutoff) of the Law Dome DE08 and DE08-2 ice cores." Available at <http://cdiac.ornl.gov/ftp/trends/co2/lawdome.smoothed.yr20> (Viewed September 9, 2008.)
- Doney, Scott C. 2006. "The Dangers of Ocean Acidification." *Scientific American* 294: 58-65.
- Fabry, V.J., B.A. Seibel, R.A. Feely, and J.C. Orr. 2008. "Impacts of ocean acidification on marine fauna and ecosystem processes." *ICES Journal of Marine Science*, 65: 414–432.
- Feely, R.A. 2008. "Ocean Acidification." In: *State of the Climate in 2007*. D. H. Levinson and J. H. Lawrimore eds. *Bulletin of the American Meteorological Society*, 89: S58. Available at: <http://www.ncdc.noaa.gov/oa/climate/research/2007/ann/bams/>
- Feely, R. A., C. L. Sabine, K. Lee, W. Berelson, J. Kleypas, V. J. Fabry, and F. J. Millero. 2004. "Impact of Anthropogenic CO₂ on the CaCO₃ System in the Oceans." *Science* 305: 362-6.
- Feely, R.A., C.L. Sabine, J.M. Hernandez-Ayon, D. Ianson, and B. Hales. 2008. "Evidence for upwelling of corrosive 'acidified' water onto the Continental Shelf." *Science* 320: 1490–1492, doi: 10.1126/science.1155676.
- Guinotte, J.M., J. Orr, S. Cairns, A. Freiwald, L. Morgan, and R. George. 2006. "Will human-induced changes in seawater chemistry alter the distribution of deep-sea scleractinian corals?" *Frontiers in Ecology and the Environment* 4(3): 141–146.

- Hall-Spencer, J.M., R. Rodolfo-Metalpa, S. Martin, E. Ransome, M. Fine, S.M. Turner, S.J. Rowley, D. Tedesco, and M. Buia. 2008. "Volcanic carbon dioxide vents show ecosystem effects of ocean acidification." *Nature* 454: 96-99. doi:10.1038/nature07051.
- Havenhand, J.N., F. Buttler, M.C. Thorndyke, and J.E. Williamson. 2008. "Near-future levels of ocean acidification reduce fertilization success in a sea urchin." *Current Biology* 18: 651-652.
- Hemleben, C., M. Spindler, and O.R. Anderson. 1989. *Modern Planktonic Foraminifera*. Springer-Verlag, Berlin, Germany. 363 pgs.
- Hoegh-Guldberg, O. P.J. Mumby, A. J. Hooten, R. S. Steneck, P. Greenfield, E. Gomez, C. D. Harvell, P. F. Sale, A. J. Edwards, K. Caldeira, N. Knowlton, C. M. Eakin, R. Iglesias-Prieto, N. Muthiga, R. H. Bradbury, A. Dubi, M. E. Hatziolos. 2007. "Coral Reefs Under Rapid Climate Change and Ocean Acidification." *Science* 318 no. 5857: 1737-1742.
- Iglesias-Rodriguez, D.M., et al. 2008. "Phytoplankton Calcification in a High-CO₂ World." *Science* 320 no. 5874: 336-340. doi:10.1126/science.1154122.
- Intergovernmental Panel on Climate Change (IPCC), 2007: Climate Change 2007: Synthesis Report. Contribution of Working Groups I, II and III to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change [Core Writing Team, Pachauri, R.K and Reisinger, A. (eds.)]. IPCC, Geneva, Switzerland, 104 pgs.
- IPCC. 2000. *Special Report on Emissions Scenarios, Working Group III, Intergovernmental Panel on Climate Change*. Edited by N. Nakicenovic et al., 595 pgs., Cambridge Univ. Press, New York.
- Kleypas, J.A., R.A. Feely, V.J. Fabry, C. Langdon, C.L. Sabine, and L.L. Robbins. 2006. *Impacts of Ocean Acidification on Coral Reefs and Other Marine Calcifiers: A Guide for Future Research*. Report of a workshop held 18–20 April 2005, St. Petersburg, FL, sponsored by NSF, NOAA, and the U.S. Geological Survey. 88 pgs.
- Kintisch, E. and E. Stokstad. "Ocean CO₂ Studies Look Beyond Coral." News article, 22 February 2008. *Science* 319:1029, reporting on unpublished data from the Hofmann Lab, University of California, Santa Barbara.
- Kübler J.E., A.M. Johnston, and J.A. Raven. 1999. "The effects of reduced and elevated CO₂ and O₂ on the weed *Lomentaria articulata*." *Plant Cell and Environment* 22: 1303–1310.
- Kuffner, I.B., A.J. Andersson, P.L. Jokie, K.S. Rodgers, and F.T. Mackenzie. 2007. "Decreased abundance of crustose coralline algae due to ocean acidification." *Nature Geoscience* 1: 114-117. doi:10.1038/ngeo100.
- Kurihara, H., and Y. Shirayama. 2004. "Effects of increased atmospheric CO₂ on sea urchin early development." *Marine Ecological Progress Series*, 274: 161–169.
- McElroy, Michael B. 2002. *The Atmospheric Environment: Effects of Human Activity*. Princeton University Press, Princeton, New Jersey. 360 pgs.
- Meehl, G.A., T.F. Stocker, W.D. Collins, P. Friedlingstein, A.T. Gaye, J.M. Gregory, A. Kitoh, R. Knutti, J.M. Murphy, A. Noda, S.C.B. Raper, I.G. Watterson, A.J. Weaver and Z.-C. Zhao. 2007. "Global Climate Projections. In: Climate Change 2007: The Physical Science Basis." Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change [Solomon, S., D. Qin, M. Manning, Z. Chen, M. Marquis, K.B. Averyt, M. Tignor and H.L. Miller (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.
- Michaelidis, B., C. Ouzounis, A. Paleras, and H.O. Pörtner. 2005. "Effects of long-term moderate hypercapnia on acid-base balance and growth rate in marine mussels *Mytilus galloprovincialis*." *Marine Ecology, Progress Series* (Vol. 293).
- Milius, S, 2008. "The next ocean: Humanity's extra CO₂ could brew a new kind of sea." *Science News*, Vol. 173#11. Available at: <http://www.sciencenews.org/view/feature/id/9479> (viewed July 1, 2008).

- Monterrey Bay Aquarium Online Field Guide. "Orange cup coral (*Balanophyllia elegans*)."
Available at http://www.mbayaq.org/efc/living_species/print.asp?inhab=152. (Viewed July 5, 2008).
- NOAA National Centers for Coastal Ocean Science (NCCOS) 2005. *A Biogeographic Assessment of the Channel Islands National Marine Sanctuary: A Review of Boundary Expansion Concepts for NOAA's National Marine Sanctuary Program*. Prepared by NCCOS's Biogeography Team in cooperation with the National Marine Sanctuary Program. Silver Spring, MD. NOAA Technical Memorandum NOS NCCOS 21. 215 pgs.
- Orr, J.C., V. J. Fabry, O. Aumont, L. Bopp, S. C. Doney, R. A. Feely, A. Gnanadesikan, N. Gruber, A. Ishida, F. Joos, R. M. Key, K. Lindsay, E. Maier-Reimer, R. Matear, P. Monfray, A. Mouchet, R. G. Najjar, G. Plattner, K. B. Rodgers, C. L. Sabine, J. L. Sarmiento, R. Schlitzer, R. D. Slater, I. J. Totterdell, M. Weirig, Y. Yamanaka, and A. Yool. 2005. "Anthropogenic ocean acidification over the twenty-first century and its impact on calcifying organisms." *Nature* 437:681-686.
- Polgar, S., S. Polefka, and A. Eastley. 2005. *A Water Quality Needs Assessment for the Channel Islands National Marine Sanctuary*. Adopted by the Sanctuary Advisory Council on September 23, 2005. Available at: <http://www.channelislands.noaa.gov/sac/pdf/10-17-05.pdf> (viewed May 2, 2008).
- Remer, L.A., NASA Earth Observatory. "What is a coccolithophore?" Online reference. Available at: <http://earthobservatory.nasa.gov/Library/Coccolithophores/printall.php> (viewed July 11, 2008).
- Riebesell, U., I. Zondervan, B. Rost, P.D. Tortell, R.E. Zeebe, and F.M. Morel. 2000. "Reduced calcification of marine phytoplankton in response to increased atmospheric CO₂." *Nature* 407: 364-7.
- Royal Society, 2005. Ocean Acidification due to Atmospheric Carbon Dioxide. Working Group members: Raven, J., K. Caldeira, H. Elderfield, O. Hoegh-Guldberg, P. Liss, U. Riebesell, J. Shepherd, C. Turley, A. Watson. The Royal Society, London. 68 pgs. Available at: <http://www.royalsoc.ac.uk> (viewed May 2, 2008). P. vi.
- Schubert, R., H.-J. Schellnhuber, N. Buchmann, A. Epiney, R. Griebhammer, M. Kulesa, D. Messner, S. Rahmstorf, J. Schmid. 2006. *The Future Oceans: Warming up, Rising High, Turning Sour*. German Advisory Council on Global Change, Special Report. Berlin. 123 pgs. Available at: http://www.wbgu.de/wbgu_home_engl.html (Viewed September 12, 2008).
- Seibel, B. A., and H.M. Dierssen. 2003. "Cascading trophic impacts of reduced biomass in the Ross Sea, Antarctica: Just the tip of the iceberg?" *The Biological Bulletin*. Vol. 205, pgs. 93-97.
- Seibel, B.A., and V.J. Fabry. 2003. "Marine biotic response to elevated carbon dioxide." *Advances in Applied Biodiversity Science* 4: 59-67.
- Shirayama Y., and H. Thornton. 2005. Effect of Increased atmospheric CO₂ on shallow water marine benthos. *Journal of Geophysical Research*, 110. C09S08, doi:10.1029/2004JC002618.
- Tans, P., NOAA Earth System Research Laboratory, Global Monitoring Division. "Recent Global Monthly Mean CO₂." September 2008. Available at <http://www.esrl.noaa.gov/gmd/ccgg/trends/> (viewed September 9, 2008).
- U.S. Environmental Protection Agency. *Quality Criteria for Water*. 1976.
- Wetmore. K.L. Wetmore. 1995. "Foraminifera: Life History and Ecology." University of California Museum of Paleontology. Available at: <http://www.ucmp.berkeley.edu/foram/foramlh.html> (viewed July 11, 2008).
- Wigley, T., R. Richels, and J. Edmonds. 1996. "Economic and environmental choices in the stabilization of atmospheric CO₂ concentration." *Nature*, 379: 242-245.