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

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

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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 CO$_2$ 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.


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.

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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 Wickett

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.

Because it harbors “an exceptionally rich and diverse biota,” 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.” 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.” Based on these mandates, the stated primary purposes of CINMS designation and resource management are “preserving and protecting this unique and fragile ecological community.”

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:

3 Id., p. 29214.
4 15 CFR 922.2(a).
5 16 U.S.C. 1431(b)(3).
“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.”

“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”;

“It is likely that anthropogenic warming over the last three decades has had a discernible influence on many natural systems”;

“With current climate change mitigation policies and related sustainable development practices, global GHG emissions will continue to grow over the next few decades”;

“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.”

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.”

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. 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, 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.

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8 Id., p. 38.
9 Id., p. 41.
10 Id., p. 44.
11 Id., p. 52.
12 Id., p. 48.
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

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].
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.
level of CO₂ could be reached within the next approximately 50 years if CO₂ emissions continue to increase at current rates. 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. 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.

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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 CO$_2$ and ocean pH**

Current atmospheric CO$_2$ concentration is approximately 385 parts per million volume (ppmv) \(^{26}\), an increase of about 100 ppmv since pre-industrial times \(^{27}\) (see Appendix 1 for NOAA’s recent global CO$_2$ 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 CO$_2$ 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 CO$_2$ in the oceans must be in equilibrium with atmospheric CO$_2$ levels. Therefore, as CO$_2$ 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 CO$_2$ 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] CO$_2$ increase is about 100x faster than has occurred over the past 650,000 years,” and “the rising atmospheric CO$_2$ levels are irreversible on human timescales,” over the next millennium the oceans will have absorbed approximately 90% of anthropogenic CO$_2$ emissions.\(^{32}\)

This ongoing uptake of anthropogenic CO$_2$ results in increased ocean acidity, signified by a drop in seawater pH; as the level of dissolved CO$_2$ increases in seawater, the concentration of hydrogen ions ([H$^+$]) increases, which reduces the pH of seawater.\(^{33}\)

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\(^{28}\) IPCC 2007. p. 37


\(^{32}\) 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: pH = –log$_{10}$ [H$^+$].

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**Ocean Acidification and CINMS: Cause, effect and response**
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.\textsuperscript{34} Since the advent of industrialization, the average pH of the ocean’s surface waters has dropped by approximately 0.1 due to anthropogenic CO\textsubscript{2} emissions (because of the logarithmic basis for pH measurement, this drop corresponds to an approximately 30\% increase in concentration of H\textsuperscript{+} ions in the world’s oceans).\textsuperscript{35} Consequently, this phenomenon of CO\textsubscript{2} absorption and elevating H\textsuperscript{+} 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 21\textsuperscript{st} century if present anthropogenic influence continues.\textsuperscript{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 CO\textsubscript{2} 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.”\textsuperscript{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.”\textsuperscript{38}

\textbf{b: Chemistry of ocean uptake of atmospheric CO\textsubscript{2}}

Close examination of the physical process by which accumulating anthropogenic, atmospheric CO\textsubscript{2} 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 CO\textsubscript{2} 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


\textsuperscript{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\textsuperscript{+}) 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\textsuperscript{+}) concentration. For example, a change in pH from 2 to 3 represents a 10-fold decrease in H\textsuperscript{+} concentration, and a shift from 2 to 4 represents a one-hundred (10 \times 10)-fold decrease in H\textsuperscript{+} concentration.” Wikipedia. “pH” http://en.wikipedia.org/wiki/PH. (Viewed May 5, 2008).


\textsuperscript{37} Caldeira and Wickett 2003.

\textsuperscript{38} The Royal Society 2005.
reagents (reacting chemicals), as well as physical variables such as pressure and temperature.  

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 Principle\textsuperscript{40}, and is central to understanding the role of anthropogenic CO\textsubscript{2} in the ocean’s chemistry and carbon cycle.

![Diagram of carbonate chemistry in seawater](image)

<table>
<thead>
<tr>
<th>Air</th>
<th>CO\textsubscript{2} (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sea Water</td>
<td>CO\textsubscript{2} (aq) + H\textsubscript{2}O \rightarrow H\textsubscript{2}CO\textsubscript{3}</td>
</tr>
<tr>
<td>CaCO\textsubscript{3} (s) (marine organisms)</td>
<td>CO\textsubscript{3}\textsuperscript{2-} + H\textsubscript{2}O \rightarrow OH\textsuperscript{-} + HCO\textsubscript{3}\textsuperscript{-}</td>
</tr>
<tr>
<td>Sea bed – Rock, Soil, Sediments</td>
<td>CaCO\textsubscript{3} (s)</td>
</tr>
</tbody>
</table>

*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 (CaCO\textsubscript{3}) in the ocean.*\textsuperscript{41}

Three forms of inorganic carbon constitute the ocean’s total dissolved inorganic carbon (DIC), and exist in the following proportions: CO\textsubscript{2} (1%); bicarbonate ions (HCO\textsubscript{3}\textsuperscript{-}) (91%), and carbonate ions (CO\textsubscript{3}\textsuperscript{2-}) (8%).\textsuperscript{42} When dissolved CO\textsubscript{2} in sea water (known as aqueous (aq) CO\textsubscript{2}) is in equilibrium with atmospheric CO\textsubscript{2}, the ongoing reaction is described

\textsuperscript{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.

\textsuperscript{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.


by the following equation, in which the rates at which CO\textsubscript{2} migrates from gas to liquid, and from liquid back to gas, are identical:\textsuperscript{43}

\[
\text{CO}_2 \text{ (gas)} \leftrightarrow \text{CO}_2 \text{ (aq)}
\]

However, dissolved CO\textsubscript{2} in the ocean reacts with seawater to drive several additional chemical processes. First, it forms carbonic acid (H\textsubscript{2}CO\textsubscript{3}), which in turn partially dissolves to produce a hydrogen ion (H\textsuperscript{+}) and a bicarbonate ion (HCO\textsubscript{3}\textsuperscript{-}). The HCO\textsubscript{3}\textsuperscript{-} may further dissociate to form another H\textsuperscript{+} and a carbonate ion (CO\textsubscript{3}\textsuperscript{2-}). Each of these reactions proceeds forward or backward, to maintain equilibrium.

\[
\text{CO}_2 \text{ (aq)} + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{CO}_3 \leftrightarrow \text{H}^+ + \text{HCO}_3^- \\
\text{HCO}_3^- \leftrightarrow \text{H}^+ + \text{CO}_3^{2-}
\]

Although some bicarbonate ions (HCO\textsubscript{3}\textsuperscript{-}) will dissociate further into carbonate (CO\textsubscript{3}\textsuperscript{2-}) and hydrogen ions (H\textsuperscript{+}) (as shown in equation III), the equilibrium state for this reaction lies far to the left, toward the production of bicarbonate (HCO\textsubscript{3}\textsuperscript{-}) ions. Therefore, this reaction can be understood as the additional formation of HCO\textsubscript{3}\textsuperscript{-} from the reaction of CO\textsubscript{3}\textsuperscript{2-} with produced hydrogen ions.

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

\[
\text{CO}_2 \text{ (g)} + \text{CO}_3^{2-} + \text{H}_2\text{O} \leftrightarrow 2\text{HCO}_3^- 
\]

In other words, as anthropogenic, dissolved CO\textsubscript{2} is forced into the system, it responds by extracting ambient carbonate (CO\textsubscript{3}\textsuperscript{2-}) and producing more bicarbonate (HCO\textsubscript{3}\textsuperscript{-}), at a rate of two molecules for everyone one molecule of the other three species), in order to restore equilibrium per Le Chatelier’s Principle.

The CO\textsubscript{3}\textsuperscript{2-} in this reaction originates from the shells and other hard structures of many organisms in the ocean, which are composed of calcium carbonate (CaCO\textsubscript{3}). Abundant CaCO\textsubscript{3} is also found in subsea geological formations and sediments. Three main forms of crystalline CaCO\textsubscript{3} 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).\textsuperscript{44}

Aragonite and high-Mg calcite are more soluble than normal calcite, which means they will dissolve and dissociate into their component ions—calcium (Ca\textsuperscript{2+}) and carbonate (CO\textsubscript{3}\textsuperscript{2-})—more readily.\textsuperscript{45}

\textsuperscript{44} Doney 2006; The Royal Society 2005.
\textsuperscript{45} Doney 2006.

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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:

\[ \text{CaCO}_3(s) \leftrightarrow \text{Ca}^{2+}(aq) + \text{CO}_3^{2-}(aq) \]  

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 solution:

\[ K_{sp} = [\text{Ca}^{2+}] \times [\text{CO}_3^{2-}] \]  

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 \( 8.7 \times 10^{-9} \) at 25°C (as mentioned above, equilibrium depends on pressure and temperature).

Depending on the concentrations of \( \text{Ca}^{2+} \) and \( \text{CO}_3^{2-} \) 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 \( \text{CO}_3^{2-} \) 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 *satisfaction state*, denoted as \( \Omega \) (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:

\[ \Omega = \frac{[\text{Ca}^{2+}] \times [\text{CO}_3^{2-}]}{K_{sp}} \]  

The higher the \( \Omega \) value, the more precipitation is promoted; the lower the \( \Omega \) value, the more dissolution of calcium carbonate into its components is promoted. For example, according to Feely et al., in oceanic regions where \( \Omega \) 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

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46 McElroy 2002.
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, \( \Omega \), 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 (\( K^* \text{sp} \)) 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 \(\text{CO}_3^{2-}\) ions, are said to be “supersaturated.” This means that they have a higher \(\Omega\), and thus will not promote dissolution of \(\text{CaCO}_3\). In contrast, “undersaturated” deep, cold water regions have a lower concentration of \(\text{CO}_3^{2-}\) and therefore promote dissolution of \(\text{CaCO}_3\) 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 \(\text{CaCO}_3\) will dissolve because there is no longer an adequate concentration of \(\text{CO}_3^{2-}\) 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 micromols\(^53\) per kilogram of sea water solution (\(\mu\)mol/kg).\(^54\) Currently, global peaks in [\(\text{CO}_3^{2-}\)], at approximately 240 \(\mu\)mol/kg, are found in the tropics. In contrast, the Southern Ocean averages 105 \(\mu\)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 (\(\text{HCO}_3^-\)) and hydrogen ions (H\(^+\)). Additional H\(^+\) ions in the water force reaction (III) further to the left, causing production of even more bicarbonate (\(\text{HCO}_3^-\)). The increase H\(^+\) concentration will drive reaction (III) to the left, causing a net consumption of carbonate ions (\(\text{CO}_3^{2-}\)) and production of bicarbonate (\(\text{HCO}_3^-\)). 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 (\(\text{HCO}_3^-\)), a decrease in that of carbonate (\(\text{CO}_3^{2-}\)), 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 [CO\(_2\)] in seawater leads to higher [H\(^+\)] and [HCO\(_3^-\)] Lower pH; and greater dissolution of geological and biological calcium carbonate (\(\text{CaCO}_3\)):

\[
\begin{align*}
1. \text{CO}_2 + \text{H}_2\text{O} & \rightarrow \text{H}_2\text{CO}_3^- \\
2. \text{H}_2\text{CO}_3 & \rightarrow \text{HCO}_3^- + \text{H}^+ \\
3. \text{H}^+ + \text{CO}_3^{2-} & \rightarrow \text{HCO}_3^-
\end{align*}
\]


\(^{51}\) 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 \(6.022 \times 10^{23}\). 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](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.
4. Then: \[ \text{CaCO}_3 \rightarrow \text{Ca}^2+ + \text{CO}_3^{2-} \]

Carbonate \((\text{CO}_3^{2-})\) concentration in seawater has already been reduced worldwide by about 16% since pre-industrial concentrations.\(^{55}\) As the “forcing” of anthropogenic \(\text{CO}_2\) on the world’s oceans continues to reduce carbonate concentration, the oceans will be able to take up atmospheric \(\text{CO}_2\) at a decreasing rate. By some estimates, the change in surface-ocean DIC per unit increase in atmospheric \(\text{CO}_2\) could be 60% lower by 2100 than it is today.\(^{56}\) Despite this decreasing rate of absorption, the concentration of \(\text{H}^+\) ions will continue to increase, causing a steady decrease in ocean \(\text{pH}\).

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 \(\text{pH}\) than surface waters. Consequently, polar and deep benthic waters are the most sensitive to anthropogenic forcing of \(\text{CO}_2\), and are understood to have already undergone significant change because of it: carbonate ion \((\text{CO}_3^{2-})\) 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 \(\text{pH}\), the ocean’s “carbonate buffer” works to counteract the increase in \(\text{H}^+\) ions.\(^{58}\) When an acid like \(\text{CO}_2\) is added to seawater, some of the \(\text{H}^+\) ions react with carbonate \((\text{CO}_3^{2-})\) to form \(\text{HCO}_3^-\), as explained in the equations above. However, as more \(\text{CO}_2\) is absorbed by the oceans, the buffering capacity diminishes because there is a reduction in the concentration of carbonate \((\text{CO}_3^{2-})\) ions, which are needed for the buffer to function.\(^{59}\)

Data produced from modeling of \(\text{CO}_2\) forcing on oceans completed at Lawrence Livermore National Laboratory suggests that the carbonate buffer functions in scenarios of gradual atmospheric \(\text{CO}_2\) change, not the rapid increase underway today.\(^{60}\) According to Caldeira (a principal investigator in the modeling study), ocean \(\text{pH}\) is demonstrated to be “relatively sensitive to added \(\text{CO}_2\)” during short-term, rapid changes in atmospheric \(\text{CO}_2\), whereas long term change (100,000 years) tends to be buffered by carbonate minerals.\(^{61}\) Their study concluded that rapid weakening of the ocean’s carbonate buffer by anthropogenic \(\text{CO}_2\) emissions “may produce changes in ocean \(\text{pH}\) greater than any... in the past 300 million years.”\(^{62}\)

Decreased concentrations of carbonate \((\text{CO}_3^{2-})\) adversely impact the precipitation of calcium carbonate \((\text{CaCO}_3)\), for example in the production of shells. As a result, there will be more dissolution of calcium carbonate \((\text{CaCO}_3)\), 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 \((\text{CO}_3^{2-})\) concentration in the world’s oceans mean that

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55 Kleypas et al. 2006.
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 $[\text{CO}_3^{2-}]$; since the 19th century it has risen by 50 to 200 meters. 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. 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 ($\Omega_{\text{arag}}$, 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 $\Omega_{\text{arag}}$ value for all coral locations in preindustrial times was 1.98 (supersaturated).” 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.

Mean $\Omega_{\text{arag}}$ values for all deep water coral locations in 2099 is 0.99 (undersaturated). 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.” 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.

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 IPCC, and various carbon dioxide emissions “stabilization
pathways” evaluated by Wigley, Richels and Edmunds (1996), 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.”

Figure 2: Estimated aragonite saturation states of the surface ocean for the years 1765, 1995, 2040, and 2100 (Feely et al. (2006), 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-

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73 Caldeira and Wickett 2005.
pH seawater that was undersaturated with respect to aragonite off Cape Mendocino near the California/Oregon border. 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.” 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.

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.

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. 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.
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, bicarbonate concentration ([HCO₃⁻]) will decrease, carbonate concentration ([CO₃²⁻]) will increase, and more CO₂ will be transferred from the oceans to the atmosphere. 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.” 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.

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⁻]. 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.”

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:

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85 Id.
86 Id.
Ocean alkalinites 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

⁸⁸ Orr et al 2005. p. 684
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.
\(^{95}\) The Royal Society 2005.
\(^{96}\) Id.
\(^{97}\) Fabry et al. 2008.
\(^{99}\) 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. 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.”

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. 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.” 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.” 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. 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
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 Emiliania 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

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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).
¹¹² Doney 2006.
foraminifera, mollusks, gastropods, and echinoderms (like urchins and sea stars).\textsuperscript{113} Benthic organisms often play important roles in ecosystems by creating habitats for other species and reducing wave power.\textsuperscript{114}

Planktonic calcifiers include both flora and fauna. For example, photosynthetic, single-celled \textit{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.\textsuperscript{115} Two key groups of calcifying fauna include the single-celled protist group \textit{foraminifera}, numerous species of which secrete calcite into shells, and euthecosomatous pteropods, swimming snails that form aragonite shells.\textsuperscript{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.\textsuperscript{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.\textsuperscript{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 CaCO\textsubscript{3} forms on pages 8 and 9), highly soluble form of calcium carbonate before transitioning to crystalline CaCO\textsubscript{3} as it matures.\textsuperscript{119} Researchers that exposed larvae of two species of urchins (\textit{Hemicentrotus pulcherrimum} and \textit{Echinodetra mathaei}) to increasing ambient carbon dioxide reported that “fertilization success, developmental rates, and larval size all decreased with increasing CO\textsubscript{2} concentration… Abnormal skeletalgenesis of the highly soluble high-magnesium CaCO\textsubscript{3} spicules in urchin larvae was also observed.”\textsuperscript{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

\textsuperscript{113} Kleypas et al 2006; The Royal Society 2005.
\textsuperscript{114} The Royal Society 2005.
\textsuperscript{116} Kleypas et al 2006.
\textsuperscript{117} Fabry et al. 2008.
\textsuperscript{118} Id., p. 426.
\textsuperscript{119} Fabry et al. 2008.
susceptible to mortality from ambient temperature change.\textsuperscript{121} Another team investigated how urchin larvae and gametes would be affected by pH levels corresponding to the year 2100 in upper-level CO$_2$ emissions scenarios; they found “significant reductions in sperm swimming speed and percent sperm motility,” and related reductions in fertilization success.\textsuperscript{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.”\textsuperscript{123}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Figure_3.jpg}
\caption{Red sea urchin (\textit{Strongylocentrotus franciscanus}), an ecologically and socioeconomically important calcifier of the Northern Channel Islands (\textit{photo}: Kirt L. Onthank).}
\end{figure}

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

\begin{thebibliography}{99}
\bibitem{Id} Id.
\end{thebibliography}
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. 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. 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). 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.

**Coral**

Coral are colonial benthic cnidarians that feed by filtering plankton out of the water. 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).

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125 Fabry et al. 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. In turn, groups of corals can accumulate to form ecologically vital coral reefs within “warm, clear shallow waters of tropical oceans worldwide.”

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. 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.

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

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129 Doney 2006.
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).\textsuperscript{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.\textsuperscript{135}

Low-latitude aragonitic corals are thought be affected most immediately by changes
experimental studies have shown that a doubling of pre-industrial [CO\textsubscript{2}]atm to 560 ppm
decreases coral calcification and growth by up to 40% through the inhibition of aragonite
formation…as carbonate-ion concentrations decrease.”\textsuperscript{136} But cold-water corals will also
suffer from decreasing calcification rates.\textsuperscript{137} In fact, the average response of corals to a
doubling of the atmospheric CO\textsubscript{2} levels is a 30% decline in calcification. Dissolution of
existing coral shells is likely to increase simultaneously.\textsuperscript{138}

\textbf{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.\textsuperscript{139} They form high-Mg calcite “shells”, and contribute to the calcification of many
reefs.\textsuperscript{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 CO\textsubscript{2} 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.”\textsuperscript{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.\textsuperscript{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.

\textbf{Foraminifera}

\textsuperscript{134} Id.
\textsuperscript{135} Id.
\textsuperscript{136} Hoegh-Guldberg et al., 2007.
\textsuperscript{137} Orr et al 2006.
\textsuperscript{138} Kleypas et al 2006.
\textsuperscript{139} Id.
\textsuperscript{140} Doney 2006.
abundance of crustose coralline algae due to ocean acidification.” Nature Geoscience 1: 114-117.
doi:10.1038/ngeo100.
\textsuperscript{142} Boxshall, A.J. 2000. “The importance of flow and settlement cues to larvae of the abalone, \textit{Haliotis}
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 tissue\(^\text{143}\). 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 CaCO\(_3\)”\(^\text{144}\). 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.”\(^\text{145}\)

There are both benthic and planktonic species of foraminifera. The planktonic forms are surface-dwelling, calcitic, heterotrophic (consumer) plankton.\(^\text{146}\) All foraminifera form high-Magnesium calcite CaCO\(_3\) during the initial stages of calcification.\(^\text{147}\) 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.\(^\text{148}\) 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 [CO\(_3^{2-}\)] in their environment.\(^\text{149}\) 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.”\(^\text{150}\)

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

**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.\(^\text{151}\) 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

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\(^{146}\) Orr et al 2005; Kleypas et al 2006.

\(^{147}\) The Royal Society 2005.

\(^{148}\) Id.


\(^{151}\) Orr et al 2005.

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Ocean Acidification and CINMS: Cause, effect and response
predatory pteropods\textsuperscript{152}, and in the biomass of pink salmon in the North Pacific\textsuperscript{153}. Shelled pteropods are major planktonic producers of aragonite shells.\textsuperscript{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.\textsuperscript{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.\textsuperscript{156}

IV. Ecosystem Effects

\textbf{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.

\textit{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 CaCO\textsubscript{3} shells/tests and are sensitive to the seawater chemistry changes previously noted (Riebesell \textit{et al.} 2000; Riebesell 2004; Orr \textit{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 CO\textsubscript{2}. 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.

\textit{Fabry et al. (2008)}:

Although the changes in seawater chemistry that result from the oceanic uptake of anthropogenic CO\textsubscript{2} 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

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\textsuperscript{153} Fabry et al., 2008, p. 426.


\textsuperscript{155} Fabry \textit{et al.} 2008.

\textsuperscript{156} Orr \textit{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

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

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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 Lab\textsuperscript{160}, 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 Cai\textsuperscript{161}, 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,

\textsuperscript{160} http://www.pmel.noaa.gov/
\textsuperscript{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 Oceans\(^{163}\)), 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) CO\(_2\) emissions reduction, and (b) management planning and coordination.

   a. Emissions reduction

      i. CINMS should pursue the completion of an audit of CO\(_2\) 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

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\(^{162}\) 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 CO\(_2\) 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](http://channelislands.noaa.gov/edu/merito.html)
this regard through the operation of its biodiesel-fueled vessels.\textsuperscript{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 CO\textsubscript{2} emissions from all activities and uses associated with the Sanctuary. This could be initiated by including CO\textsubscript{2} 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 CO\textsubscript{2}-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.

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

### Appendix 2

Table excerpted from Fabry et al. 2008\(^{165}\): “Examples of the response of marine fauna to ocean acidification” [continued on following page].

<table>
<thead>
<tr>
<th>Species</th>
<th>Description</th>
<th>CO(_2) system parameters</th>
<th>Sensitivity</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Planktonic foraminifera</strong></td>
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<td></td>
</tr>
<tr>
<td><em>Orbulina universa</em></td>
<td>Symbiote-bearing</td>
<td>pCO(_2) 560 – 780 ppmv</td>
<td>8 – 14% reduction in shell mass</td>
<td>Spero et al. (1997); Bijma et al. (1999, 2002)</td>
</tr>
<tr>
<td><strong>Cnidaria</strong></td>
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<tr>
<td><em>Scyphozoa</em></td>
<td>Jellyfish</td>
<td>North Sea seawater pH drop</td>
<td>Increase in frequency as measured by CPR from 1958 to 2000</td>
<td>Atrill et al. (2007)</td>
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<tr>
<td></td>
<td></td>
<td>from 8.3 to 8.1</td>
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<tr>
<td><strong>Mollusca</strong></td>
<td></td>
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<tr>
<td><em>Clio pyramulida</em></td>
<td>Shelled pteropod</td>
<td>(\Delta\text{pH}&lt;0.1)</td>
<td>Shell dissolution</td>
<td>Feely et al. (2004); Orr et al. (2005); this work</td>
</tr>
<tr>
<td><em>Haliotis leucogaster</em></td>
<td>Greenlip abalone</td>
<td>pH 7.8; pH 7.39</td>
<td>5% and 50% growth reductions</td>
<td>Harris et al. (1999).</td>
</tr>
<tr>
<td><em>Haliotis rubra</em></td>
<td>Blacklip abalone</td>
<td>pH 7.93; pH 7.37</td>
<td>5% and 50% growth reductions</td>
<td></td>
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<td><em>Mytilus edulis</em></td>
<td>Mussel</td>
<td>pH 7.1 / 10 000 ppmv</td>
<td>Shell dissolution</td>
<td>Lindinger et al. (1984)</td>
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<tr>
<td><em>Crassostrea gigas</em></td>
<td>Oyster</td>
<td>pCO(_2) 740 ppmv</td>
<td>25% decrease in calcification rate</td>
<td>Gazeau et al. (2007)</td>
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<tr>
<td><em>Mytilus galloprovincialis</em></td>
<td>Mediterranean mussel</td>
<td>pH 6.3 – 5000 ppmv</td>
<td>10% decrease in calcification rate</td>
<td>Michaelidis et al. (2005)</td>
</tr>
<tr>
<td><em>Placopecten magellanicus</em></td>
<td>Giant scallop</td>
<td>pH &lt; 8.0</td>
<td>Decrease in fertilization and embryo development</td>
<td>Desrochers et al. (1996)</td>
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<tr>
<td><em>Tivela stultorum</em></td>
<td>Pismo clam</td>
<td>pH &lt; 8.5</td>
<td>Decrease in fertilization rates</td>
<td>Avalarado-Alvarez et al. (1996)</td>
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<tr>
<td><em>Pinctada fucata</em></td>
<td>Japanese pearl</td>
<td>pH 7.7</td>
<td>Shell dissolution, reduced growth</td>
<td>Reviewed in Knutzen (1981)</td>
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<tr>
<td><em>Meretrix meretrix</em></td>
<td>Oyster</td>
<td>pH &gt; 7.4</td>
<td>Increasing mortality</td>
<td>Green et al. (2004)</td>
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<tr>
<td><em>Illex Illecebrosus</em></td>
<td>Clam</td>
<td>(\Delta\text{pH}=0.3)</td>
<td>Juvenile shell dissolution leading to increased mortality</td>
<td></td>
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<tr>
<td><em>Dosidicus gigas</em></td>
<td>Epipelagic squid</td>
<td>2000 ppmv</td>
<td>Impaired oxygen transport</td>
<td>Fütter and Reipschläger (1996)</td>
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<tr>
<td><em>Arthropoda</em></td>
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<tr>
<td><em>Acartia aukia</em></td>
<td>Copepod</td>
<td>0.2 – 1% CO(_2)</td>
<td>Decrease in egg hatching success; increase in nauplius mortality rate; increasing mortality with increasing CO(_2) concentration and duration of exposure</td>
<td>Kurihara et al. (2004)</td>
</tr>
<tr>
<td><em>Copepods</em></td>
<td></td>
<td>~2000 – 10 000 ppmv</td>
<td></td>
<td>Watanabe et al. (2006)</td>
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<td><em>Euphausia pacifica</em></td>
<td>Krill</td>
<td>pH &lt; 7.6</td>
<td>Mortality increased with increasing exposure time and decreasing pH</td>
<td>Yamada and Ikeda (1999)</td>
</tr>
<tr>
<td><em>Pterochaeta longata</em></td>
<td>Mesopelagic copepod</td>
<td>pH &lt; 8.0</td>
<td></td>
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<tr>
<td><em>Cancer pagurus</em></td>
<td>Ostracod</td>
<td>1% CO(_2) ~10 000 ppmv</td>
<td>Reduced thermal tolerance, aerobic scope</td>
<td>Matzger et al. (2007)</td>
</tr>
<tr>
<td><em>Chaetognatha</em></td>
<td>Sagitta elegans</td>
<td>pH &lt; 7.6</td>
<td>Mortality increased with increasing exposure time and decreasing pH</td>
<td>Yamada and Ikeda (1999)</td>
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<tr>
<td><em>Echinodermata</em></td>
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<tr>
<td><em>Psammocentrotus micraster</em></td>
<td>Sea urchin</td>
<td>~500 – 10 000 ppmv</td>
<td>Decreased fertilization rates; impacts larval development</td>
<td>Spicer (1995); Miles et al. (2007)</td>
</tr>
<tr>
<td><em>Hemicentrotus pulcherinus</em></td>
<td>Sea urchin</td>
<td>pH 7.8</td>
<td></td>
<td>Kurihara and Shirayama (2004)</td>
</tr>
<tr>
<td><em>Echinometra mathaei</em></td>
<td>Deep-sea urchin</td>
<td>pH 7.8</td>
<td>80% mortality under simulated CO(_2) sequestration</td>
<td>Barry et al. (2002)</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Species</th>
<th>Description</th>
<th>$\text{CO}_2$ system parameters</th>
<th>Sensitivity</th>
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<td><strong>Sipuncula</strong></td>
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<tr>
<td>Sipunculus nudus</td>
<td>Peanut worm</td>
<td>1% CO$_2$, 10 000 ppmv</td>
<td>Metabolic suppression</td>
<td>Portner and Reipschlager (1996)</td>
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<td><strong>Vertebrata</strong></td>
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<tr>
<td>Scyliorhinus canicula</td>
<td>Dogfish</td>
<td>pH 7.7, 0.13% CO$_2$ 7% CO$_2$, ~70 000 ppmv</td>
<td>Increased ventilation</td>
<td>Reviewed in Truchon (1987)</td>
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<td></td>
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<td>Hayashi et al. (2004)</td>
</tr>
<tr>
<td>Sillago japonica</td>
<td>Japanese whiting</td>
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<td>Rapid mortality in 1-step exposure</td>
<td>Kikkawa et al. (2006)</td>
</tr>
<tr>
<td>Paralichthys olivaceus</td>
<td>Japanese flounder</td>
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<td>100% mortality within 48 h</td>
<td>Hayashi et al. (2004)</td>
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<tr>
<td>Euthynnus affinis</td>
<td>Eastern little tuna</td>
<td>pH 7.7, 0.13% CO$_2$ 7% CO$_2$, ~70 000 ppmv</td>
<td>100% mortality of eggs after 24 h</td>
<td>Kikkawa et al. (2003)</td>
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<td>Pogonus major</td>
<td>Red sea bream</td>
<td>pH 7.7, 0.13% CO$_2$ 7% CO$_2$, ~70 000 ppmv</td>
<td>&gt;60% larval mortality after 24 h</td>
<td>Ishimatsu et al. (2005)</td>
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<td>Yellowtail/</td>
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<td>Reduced cardiac output, 100% mortality after 8 h</td>
<td>Ishimatsu et al. (2004)</td>
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<td>amberjack</td>
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<td>Sparus aurata</td>
<td>Mediterranean fish</td>
<td>pH 7.3, ~5000 ppmv</td>
<td>Reduced metabolic capacity</td>
<td>Michaelidis et al. (2007)</td>
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<td>Dicentrarchus labrax</td>
<td>Sea bass</td>
<td>pH 7.35, 24 mg L$^{-1}$ CO$_2$</td>
<td>Reduced feed intake</td>
<td>Cecchini et al. (2001)</td>
</tr>
</tbody>
</table>
Works Cited


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