SPECIAL ISSUE FEATURE

BY SCOTT C. DONEY, WILLIAM M. BALCH, VICTORIA J. FABRY, AND RICHARD A. FEELY

OCEAN ACIDIFICATION

A CRITICAL EMERGING PROBLEM FOR THE OCEAN SCIENCES

ABSTRACT

Over a period of less than a decade, ocean acidification—the change in seawater chemistry due to rising atmospheric carbon dioxide (CO_2) levels and subsequent impacts on marine life—has become one of the most critical and pressing issues facing the ocean research community and marine resource managers alike. The objective of this special issue of *Oceanography* is to provide an overview of the current scientific understanding of ocean acidification as well as to indicate the substantial gaps in our present knowledge. Papers in the special issue discuss the past, current, and future trends in seawater chemistry; highlight potential vulnerabilities to marine species, ecosystems, and marine resources to elevated CO_2; and outline a roadmap toward future research directions. In this introductory article, we present a brief introduction on ocean acidification and some historical context for how it emerged so quickly and recently as a key research topic.

BACKGROUND

When we burn gasoline in our cars, use electricity from burning natural gas or coal at power plants, or chop down and burn tropical forests for new agricultural land, we release carbon dioxide (CO_2) gas into the air. The quantity of carbon released by human activities is enormous. For 2008, the most recent year for which we have published data, total human CO_2 emissions were about 10 billion tons of carbon annually (equivalent to one million tons per hour or, on a per capita basis, ~ 0.2 kg person^{-1} h^{-1}; note that 1 billion tons equals 1 Pg or 1 x 10^{15} g). Of this amount, 8.7 ± 0.5 billion tons originates from fossil fuel combustion and cement production and another 1.2 ± 0.7 billion tons from deforestation (Le Quéré et al., 2009). The cumulative human CO_2 emissions over the industrial era now amount to close to 560 billion tons. A little less than half of this anthropogenic CO_2 remains in the atmosphere—certainly enough to be of grave concern as a greenhouse gas leading to climate change. The remainder is, at present, removed in roughly equal parts into the ocean and by land vegetation. Revelle and Suess (1957) wrote a prophetic view of our perturbations to the global carbon cycle: *Thus human beings are now carrying out a large scale geophysical experiment of a kind that could not have happened in the past nor be reproduced in the future*—a sentiment that may be especially true for ocean acidification.

The build-up of excess CO_2 in the atmosphere is clearly evident in time series such as the one established in 1958 by Charles David Keeling from the top of Mauna Loa volcano in Hawaii, the longest atmospheric CO_2 instrumental record. When Keeling started making measurements, atmospheric CO_2 was about 315 parts per million (ppm)

(Keeling, 1960); present values (387 ppm) are already more than 37% greater than pre-industrial levels (~ 280 ppm) (Feely et al., 2009; Tans, 2009). If fossil fuel consumption continues unabated, it could double or triple before the end of this century (Tans, 2009). The current rapid rise in atmospheric CO_2 is as much as 30 times faster than natural rates in the geological past, and present levels are higher than at anytime in at least the last 850,000 years and likely several million years (Kump et al., 2009).

As atmospheric CO_2 rises, thermodynamics and air-sea gas transfer processes drive some of the extra CO_2 into ocean surface waters, leading to substantial shifts in seawater acid-base chemistry and, importantly, the chemical speciation of the large reservoir of inorganic carbon dissolved in seawater (Figure 1). In aggregate, these chemical changes are termed "ocean acidification." The basic principles for these reactions have been appreciated for some time, and even before the start of the Mauna Loa record, Revelle and Suess (1957) argued that the ocean would quite effectively remove a large fraction of fossil fuel CO_2 from the atmosphere (see also Bolin and Eriksson, 1959).

The basic chemistry of ocean acidification was first described in the early 1970s, based on early models of CO_2 exchange at the air-sea interface and the thermodynamics of the carbon system in seawater (Broecker et al., 1971, 1979; Broecker and Takahashi, 1977; Fairhall, 1973; Zimen and Altenhein, 1973; Whitfield, 1974; Skirrow and Whitfield, 1975; Pytkowicz and Small, 1977). Although these early authors all presented calculations to show that CO_2 emissions would likely cause undersaturation with respect to aragonite and calcite at some point, their estimates of when this might happen varied greatly because of a lack of agreement on carbon system equilibrium in seawater at that time. As more laboratory and field results were published in the 1980s, it became clear that the high-latitude regions of the ocean would first become undersaturated with respect to aragonite sometime in the twenty-first century (Feely and Chen, 1982; Mucci, 1983; Byrne et al., 1984; Feely et al., 1984, 1988) and that tropical regions would remain supersaturated with respect to these minerals throughout the twenty-first century.

By the 1990s, an intense effort of ship-based surveys and ocean time series was underway to quantify the ocean's role in the climate system as a sink for human-released CO_2 (Sabine et al., 2004). Now, the alteration of seawater chemistry from the invasion of excess CO_2 into the ocean is also clear from these ongoing field observations (Dore et al., 2009; Fabry et al., 2009; Feely et al., 2009; Hauri et al., 2009). The analytical methods for seawater carbonate chemistry are now well established (Dickson et al., 2007). Coordinated observational strategies for monitoring ocean acidification (and its potential biological impacts; see below) are underway (Feely et al., in open review), applying traditional techniques as well as new approaches that employ satellite remote sensing (Gledhill et al., 2009; Balch and Utgoff, 2009) and autonomous platforms such as floats and gliders (Johnson et al., 2009; Bishop, 2009).

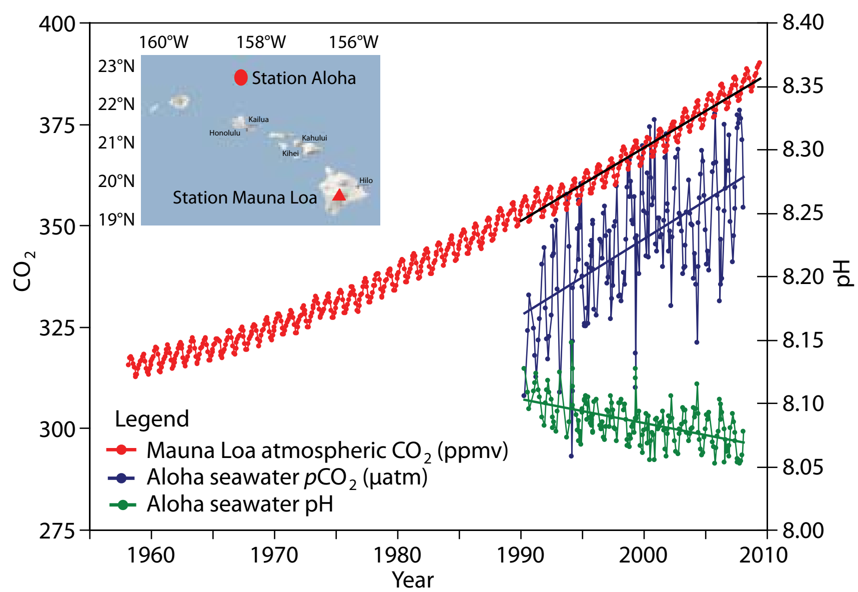

Figure 1: Time series of atmospheric CO_2 at Mauna Loa (in parts per million volume, ppmv; red), surface ocean pCO_2 (μatm; blue) and surface ocean pH (green) at Ocean Station ALOHA in the subtropical North Pacific Ocean. Note that the increase in oceanic CO_2 over the past 17 years is consistent with the atmospheric increase within the statistical limits of the measurements. *Mauna Loa data courtesy of Pieter Tans, National Oceanic and Atmospheric Administration/Earth System Research Laboratory (http://www.esrl.noaa.gov/gmd/ccgg/trends); Hawaii Ocean Time-Series (HOT)/ALOHA data courtesy of David Karl, University of Hawaii (http://hahana.soest.hawaii.edu; see also Dore et al., 2009)*

Concerns also arose about how marine ecosystems might respond to ocean warming and changes in circulation caused by alterations in the planet's radiative balance from the elevated CO_2 in the atmosphere (Boyd and Doney, 2002). By contrast, the biological effects of rising atmospheric and oceanic CO_2 directly on marine life was a rather obscure topic through much of the 1980s and early 1990s, explored by only a few scientists. Several groundbreaking studies, specifically designed to test atmospheric CO_2 impacts, revealed potentially dramatic responses in corals and coral reef communities (e.g., Gattuso et al., 1998; Marubini and Atkinson, 1999; Kleypas et al., 1999; Langdon et al., 2000) and planktonic organisms (e.g., Riebesell et al., 2000). Broad interest and visibility on the topic were spurred by an influential Royal Society report (Royal Society, 2005) and the 2004 Symposium on the Ocean in a High-CO_2 World (Orr et al., 2009). Toward the end of this decade, there is now striking evidence from the laboratory and field that many marine species may be affected by ocean acidification (e.g., see recent review papers: Kleypas et al., 2006; Fabry et al., 2008; Guinotte and Fabry, 2008; Doney et al., 2009; Kleypas and Yates, 2009).

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BIOLOGICAL IMPACTS

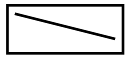
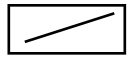
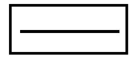
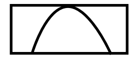
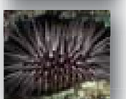
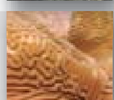
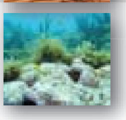
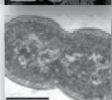
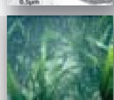
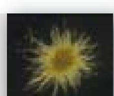
Unlike the case for terrestrial plants, many marine phytoplankton species are not limited by aqueous CO_2 gas concentrations, having developed biochemical techniques for concentrating CO_2 inside their cells or by tapping into the much larger seawater pool of dissolved inorganic carbon (e.g., Tortell et al., 1997). Recent work, however, suggests that photosynthesis rates of some cyanobacteria may be enhanced under elevated aqueous CO_2, especially in conjunction with warming, and that there may be a wide range of possible effects on nutrient cycling, including increased nitrogen fixation rates (Hutchins et al., 2009). Phytoplankton growth may also be influenced by CO_2-driven changes in acid-base chemistry and trace metal availability (Millero et al., 2009). Similarly, the pH gradient across cell membranes is coupled to numerous critical physiological/biochemical reactions within marine organisms, ranging from such diverse processes as photosynthesis, to nutrient transport, to respiratory metabolism. The impact of ocean acidification (and changing pH gradients) on this biochemistry is barely understood (Figure 2).

Increased solubility of calcium carbonate minerals used as skeleton and shell material by corals (Cohen and Holcomb, 2009; Kleypas and Yates, 2009) and other pelagic and benthic calcifiers (Fabry et al., 2009a, 2009b; Balch and Utgoff, 2009) generally results in a slowdown of the overall calcification process by mechanisms that are just beginning to be understood (Cohen and Holcomb, 2009). In fact, the response of calcifying organisms to ocean acidification may be more varied than first thought, as indicated in recent experiments showing elevated calcification rates for some taxa under higher CO_2 (Ries et al., 2009). Decreased calcification could have negative impacts on marine ecosystems, with consequent effects on local marine fisheries and coastal protection from storms. The abundance of commercially important shellfish species (i.e., clams, oysters, sea urchins) could also decline, which could have serious consequences for marine food resources (Cooley et al., 2009).

PHYSICAL IMPACTS

A generally unappreciated physical impact of ocean acidification is the reduction of low-frequency sound adsorption because of the pH-dependent decline in dissolved borate ions (Brewer and Hester, 2009). As noted by Brewer and Hester (2009), the effect can be significant: "a decline in pH of only 0.3 causes a 40% decrease in the intrinsic sound absorption coefficient (α, dB km^{-1})." Nevertheless, the environmental consequences of increased "noise" in the ocean, particularly with respect to whales and other marine mammals, is largely unknown.

Along with sound propagation, light propagation might also be affected. In a "decalcified" ocean, devoid of the ubiquitous calcium carbonate particles such as microscopic coccoliths, light scattering and attenuation would be reduced, resulting in deeper euphotic zones. This scenario could have consequences for such biogeochemical aspects as export

PHYSIOLOGICAL RESPONSE		MAJOR GROUP	# SPECIES STUDIED	RESPONSE TO INCREASING CO_2 a 	b 	c 	d 
CALCIFICATION							
		Coccolithophores	4	2	1	1	1
		Planktonic Foraminifera	2	2	–	–	–
		Molluscs	6	5	–	1	–
		Echinoderms	3	2	1	–	–
		Tropical Corals	11	11	–	–	–
		Coralline Red Algae	1	1	1	–	–
PHOTOSYNTHESIS[1]							
		Coccolithophores[2]	2	–	2	2	–
		Prokaryotes	2	–	1	1	–
		Seagrasses	5	–	5	–	–
NITROGEN FIXATION							
		Cyanobacteria	4	–	3	1	–
REPRODUCTION							
		Molluscs	4	4	–	–	–
		Echinoderms	1	1	–	–	–

[1] Strong interactive effects with nutrient and trace metal availability, light, and temperature
[2] Under nutrient replete conditions

Figure 2. Representative examples of impacts of ocean acidification on major groups of marine biota derived from experimental manipulation studies. The response curves on the right indicate four cases: (a) linear negative, (b) linear positive, (c) level, and (d) nonlinear parabolic responses to increasing levels of seawater pCO_2 for each of the groups. *Adapted from Doney et al. (2009)*

BOX 1. ORGANIZATIONS DEVOTING SIGNIFICANT RESOURCES TO OCEAN ACIDIFICATION

SCIENTIFIC RESEARCH CONSORTIA

The European Project on Ocean Acidification (EPOCA)

http://www.epoca-project.eu

A consortium of European researchers examining ocean acidification's progress and effects on marine life, and using scientific results to develop educational materials for stakeholders.

Integrated Marine Biogeochemistry and Ecosystem Research (IMBER)/Surface Ocean Lower Atmosphere Study (SOLAS) Joint Carbon Working Group

http://www.imber.info/C_WG_SubGroup3.html

A working group composed of international researchers tasked with coordinating and synthesizing ocean acidification research activities worldwide.

International Geosphere-Biosphere Programme (IGBP) and the Scientific Committee on Oceanic Research (SCOR) Fast Track Initiative

http://igbp-scor.pages.unibe.ch

A research consortium of international researchers studying ocean acidification from a paleoenvironmental perspective

Marine Climate Change Impacts Partnership (MCCIP)

http://www.mccip.org.uk

A coordinating body of United Kingdom-based researchers cooperating to provide information to decision makers.

Ocean Carbon and Biogeochemistry (OCB) Office

http://www.us-ocb.org

A United States-based coordinating body composed of scientific researchers tasked with promoting dialogue and collaboration among researchers and developing educational materials in support of national funding agencies' goals.

NONPROFIT ORGANIZATIONS

Natural Resources Defense Council

http://www.nrdc.org/oceans/acidification/default.asp

A United States-based environmental action group working to protect Earth's natural assets.

Ocean Conservancy

http://www.oceanconservancy.org

A United States-based conservation organization dedicated to educating citizens about the current challenges facing ocean ecosystems and promoting conservation-based legislation.

EDUCATIONAL ORGANIZATIONS

CarboSchools

http://www.carboeurope.org/education

EPOCA-affiliated organization promoting partnerships between researchers and secondary educators and facilitating several regional projects designed to help students connect climate change issues with their local environment.

Center for Microbial Oceanography: Research and Education (C-MORE)

http://cmore.soest.hawaii.edu/index.htm

A consortium of American institutions bringing together scientists, educators, and communities to highlight the importance of marine microbes.

BOX 2. INFORMATION ABOUT OCEAN ACIDIFICATION

EDUCATIONAL TOOLS

Acid Test: The Global Challenge of Ocean Acidification

http://www.nrdc.org/oceans/acidification/aboutthefilm.asp

NRDC-produced short documentary narrated by Sigourney Weaver providing an overview of ocean acidification.

C-MORE Ocean Acidification Teaching Module

http://cmore.soest.hawaii.edu/education/teachers/science_kits/ocean_acid_kit.htm

Three-lesson kit for grades 6–12 including DVD, presentations, worksheets, and experiment materials that can be borrowed from a C-MORE partner institution.

OCB Ocean Acidification Lab Kit

http://www.us-ocb.org/publications/OCB-OA_labkit102609.pdf

OCB-produced lab kit for teachers of grades 5–12 providing complete plans, worksheets, and shopping lists for two inexpensive laboratory activities and one demonstration.

Acid Ocean Virtual Lab

http://i2i.stanford.edu/carbonlab/co2lab.swf

Stanford University-developed online laboratory activities teaching about ocean acidification's impact on marine organisms, especially sea urchins.

NEWS

http://oceanacidification.wordpress.com/

EPOCA maintains a blog, updated nearly every day, containing news and abstracts about ocean acidification, and links to ocean acidification coverage in the media.

http://iodeweb3.vliz.be/oanet/index.html

The Ocean Acidification Network collects information for the scientific community about ocean acidification.

BRIEFINGS, FACT SHEETS, AND HELPFUL INFORMATION

European Science Foundation Science Policy Briefing: Impacts of Ocean Acidification

http://www.esf.org/publications/policy-briefings.html

EUR-Oceans Ocean Acidification Fact Sheet

http://www.eur-oceans.info/EN/education/pdf/FS7_ocean%20acidification.pdf

EPOCA Guide To Best Practices in Ocean Acidification Research and Data Reporting

http://www.epoca-project.eu/index.php/Home/Guide-to-OA-Research

(Draft available now, final document expected early 2010)

The Honolulu Declaration on Ocean Acidification and Reef Management

http://www.nature.org/wherewework/northamerica/states/hawaii/files/final_declaration_with_appendices.pdf

National Oceanic and Atmospheric Administration Ocean Acidification Fact Sheet and Web Site

http://www.pmel.noaa.gov/co2/OA/Ocean_Acidification%20FINAL.pdf

http://www.pmel.noaa.gov/co2/OA

The Ocean in a High-CO_2 World: Ocean Acidification Summary for Policymakers from SCOR, UNESCO, IGBP, and IAEA (Also known as "The Monaco Declaration")

http://ioc3.unesco.org/oanet/OAdocs/SPM-lorezv2.pdf

MOVIES ON OCEAN ACIDIFICATION

Natural Resource Defense Council Web Site On Ocean Acidification

http://www.nrdc.org/oceans/acidification

http://www.nrdc.org/oceans/acidification/aboutthefilm.asp

"A Sea Change"

http://www.aseachange.net

production (Balch and Utgoff, 2009). It is not a stretch of the imagination to assume that the physical chemistry of seawater will change such that rates of redox reactions associated with metal oxidation and electolysis would change. This more applied chemistry would be of strategic importance to both shipping and naval interests, particularly as it affects the integrity of ship hulls.

NATIONAL AND INTERNATIONAL RESPONSE TO OCEAN ACIDIFICATION

Over the last several years, the rapid pace of scientific discoveries has led to a dramatic rise in the visibility of, concern about, and urgency of ocean acidification. Nongovernmental organizations are issuing communiqués and declarations, and research programs on ocean acidification are being launched around the world at national and international levels (e.g., the European Project on Ocean Acidification [EPOCA] in the European Union; Gattuso et al., 2009; http://www.epoca-project.eu/; Orr et al., 2009). EPOCA has also developed a *Guide for Best Practices in Ocean Acidification Research and Data Reporting* for conducting research on ocean acidification under controlled laboratory conditions (Box 3; Riebesell et al., in press). In the United States, a key scientific workshop on the topic was organized under the Ocean Carbon and Biogeochemistry (OCB) Program (http://us-ocb.org/; Fabry et al., 2009b). Following the passage of the Federal Ocean Acidification Research And Monitoring (FOARAM) Act of 2009 (Public Law 111-11), the United States is formulating its own strategy for an integrated national research program on

BOX 3. GUIDE TO BEST PRACTICES IN OCEAN ACIDIFICATION RESEARCH AND DATA REPORTING

BY ULF RIEBESELL, VICTORIA J. FABRY, LINA HANSSON, AND JEAN-PIERRE GATTUSO

Growing concern about the effects of ocean acidification on marine organisms and ecosystems has stimulated a wide range of research activities over the past few years. With new national and international programs recently started and others still in preparation, research aimed at detecting potential effects of ocean acidification on various processes and organisms will increase in the coming decade. Due to the cross-cutting nature of the scientific problem, research on ocean acidification brings together a spectrum of disciplines, from paleo- and chemical oceanography, to marine biogeochemistry and climate modeling, to marine ecology, physiology, and molecular and evolutionary biology. The various scientific communities have their own disciplinary heritage, and frequently use specific terminology, research approaches, and methodologies. Moreover, with new funding opportunities now becoming available for ocean acidification research, many researchers, postdoctoral investigators, and PhD students with no or limited previous experience in ocean acidification research will enter the field. To ensure comparability of the vast amount of data generated in this rapidly expanding field of marine sciences and to achieve the highest possible data quality, it is important to agree on standardized protocols for observational and experimental approaches, carbonate chemistry manipulations and measurements, and data reporting.

In November 2008, the European Project on Ocean Acidification (EPOCA) and the International Oceanographic Commission (IOC) of UNESCO, organized an international workshop in Kiel, Germany,

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on Best Practices in Ocean Acidification Research. The workshop received funding from the Scientific Council on Oceanic Research (SCOR), the US Ocean Carbon Biogeochemistry program (OCB), and the Kiel Excellence Cluster *The Future Ocean*. The meeting brought together about 40 scientists from the European Union, United States, Japan, Korea, China, and Australia with expertise in different areas of ocean acidification research. Workshop participants reviewed best practices in this field and prepared an outline for a guide that served as a basis to produce—with the help of additional invited experts—a comprehensive set of guidelines on ocean acidification research[1].

After a first round of anonymous expert reviews, revised sections were made available online for four months of open access community review starting in May 2009. Based on the comments and input of the international scientific community and the assigned chapter editors, the sections were further revised (drafts available at http://www.epoca-project.eu/index.php/Best-Practices-Guide/). Notation, style, and structure were harmonized in a final round of editing by the chief editors. The *Guide to Best Practices in Ocean Acidification Research and Data Reporting* will be published as an EU report and made available online in early 2010. Its recommendations will be presented to the wider community, with a special emphasis on students and scientists new to ocean acidification research, in training workshops to be conducted within the framework of existing and upcoming ocean acidification projects. It is envisioned that the guide's recommendations will be revisited and—where appropriate—further refined in a few years as understanding of ocean acidification advances and new techniques and approaches emerge.

[1] It is recognized that the paleosciences will continue to provide important contributions to unraveling the consequences of ocean acidification. However, this field entails another broad spectrum of scientific approaches not covered in this guide to best practices. The paleo community may find it beneficial to formulate guidelines and standardized protocols specific for research on past acidification events.

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ocean acidification (National Research Council, in press).

Ocean acidification is inherently an interdisciplinary topic, as reflected in the crosscutting nature of the papers in this issue. Relevant subject matters range from seawater carbonate, to acid-base and physical chemistry, to organismal physiology, food web dynamics, and biogeochemistry. Time scales span the geological record for the last 500 million years to the recent historical past and extend to projections for the near-term future of the twenty-first century and beyond. Unlike many other human perturbations to the marine environment, ocean acidification is widely distributed and will influence many biogeographic regions, including open-ocean planktonic systems, coastal upwelling zones, coral reefs, high latitudes, benthic environments, and the deep sea. Ocean acidification is stimulating research in areas ranging from basic, unresolved questions on the biochemistry of biomineralization (shell and skeleton formation from carbonate minerals) to the socio-economic impacts on marine fisheries, aquaculture, and other ecosystem services.

Unless there are dramatic changes in fossil fuel use, projected human-driven ocean acidification over this century will be larger and more rapid than anything affecting sea life for tens of millions of years. And the problem will be with us for a long time because it takes centuries to thousands of years for natural processes, primarily mixing into the deep-sea and increased dissolution of marine carbonate sediments, to remove excess carbon dioxide from the air. Future ocean acidification also will occur in conjunction with other human-driven stresses like global warming, pollution, overfishing, and coastal nutrient inputs. The solutions to ocean acidification are clear—slowing and eventually eliminating fossil fuel carbon emissions and, perhaps on longer time scales, developing approaches for removing excess carbon dioxide from the atmosphere.

ACKNOWLEDGEMENTS

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