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Detecting the Unexpected: A Research Framework for Ocean Acidification

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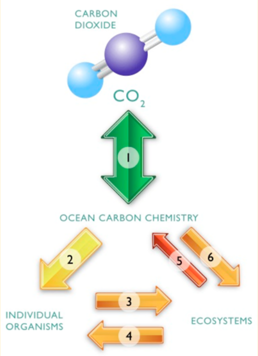
ABSTRACT: The threat that ocean acidification (OA) poses to marine ecosystems is now recognized and U.S. funding agencies have designated specific funding for the study of OA. We present a research framework for studying OA that describes it as a biogeochemical event that impacts individual species and ecosystems in potentially unexpected ways. We draw upon specific lessons learned about ecosystem responses from research on acid rain, carbon dioxide enrichment in terrestrial plant communities, and nitrogen deposition. We further characterize the links between carbon chemistry changes and effects on individuals and ecosystems, and enumerate key hypotheses for testing. Finally, we quantify how U.S. research funding has been distributed among these linkages, concluding that there is an urgent need for research programs designed to anticipate how the effects of OA will reverberate throughout assemblages of species.



INTRODUCTION

Rising atmospheric CO_2 is linked to global warming and changes to terrestrial ecosystems.[1] In the oceans, increasing CO_2 alters surface seawater chemistry by decreasing ocean pH and calcium carbonate saturation state.[2,3] Collateral changes in biological systems are already apparent[4] and further alterations are expected. While there is no clear boundary between the role of CO_2 in Earth's climate and its role in seawater chemistry, the term ocean acidification (OA) is used to refer to the subset of changes in ocean chemistry that propagate from the addition of anthropogenic CO_2 to seawater. On time scales shorter than centuries, the primary concern with OA is a potential reconfiguration of marine ecosystems.[5]

We suggest a research framework to guide efforts toward anticipating and projecting biological changes from OA over the coming decades to centuries. Our efforts were part of an OA Principal Investigator's Meeting sponsored by the National Science Foundation for those currently receiving OA funding from Federal funding sources within the USA. We review several past investigations into ecosystem impacts—across disparate ecosystems—and take from them lessons that we can apply to research emerging OA phenomenon. Drawing from

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these lessons, we develop a framework for integrating the effect of feedbacks between carbon chemistry changes, individual species, and ecosystems. We also use the opportunity to identify and highlight central hypotheses that need testing.

Past ecosystem-level research provides lessons that can aid future efforts to study environmental change. We look to studies of multiple ecosystems to anticipate results and formulate a conceptual framework. Specifically, we cite three case studies of the effects of environmental change on ecosystems and argue that these studies motivate a system-level approach to the study of OA.

■ PREVIOUS ECOLOGICAL OBSERVATIONS THAT INFORM OA RESEARCH

The first key observation from other ecological studies is that assays and experiments with single species do not necessarily predict the responses of multispecies systems. For example, an assemblage of terrestrial plants utilizes nitrogen more completely than predicted by single-species assays of nitrogen use.[6] Thus, a diverse plant community ameliorates the effects of anthropogenic nitrogen deposition by reducing accumulation in soil. A comparison of ocean warming effects on species in situ also had a cautionary message. Along the California Current system, artificial warming of seawater by a power plant was predicted to have a positive effect on species with a southerly geographic range and a more negative effect on those with a northerly range. However, the observed species response was uncorrelated with their geographic ranges; instead, their response was suggested to be caused by species interactions.[7] Analogously, a species that is negatively affected by OA at the individual level may ultimately benefit from OA due to indirect effects, such as decreases in the abundance of a competitor or consumer. Because studies of environmental change in the ocean will likely reveal such emergent properties—or properties that are only apparent when component parts are joined together[8]—research programs should be prepared to detect them.

A second key observation is that structural and functional properties of a system may not respond similarly. Experimental studies of acid rain into lakes revealed that the species composition of primary producers changed while their productivity (e.g., a function) remained unchanged.[9] Thus, manipulation of a community allowed compensatory responses by some members previously at low density. We need to ask how ecosystem function changes with OA, including any direct or indirect effects on the fitness of key species.

A third key observation is that the response of an ecosystem can change through time and may include lagged responses. Terrestrial FACE (free-air CO_2 enrichment) experiments in plant communities showed an initial increase in net primary productivity as CO_2 increased, followed by an eventual decline. The lagged decline in productivity is consistent with the progressive nitrogen limitation hypothesis, where nitrogen eventually begins to limit primary productivity. Thus, only after 6 years of forest development did it become apparent that primary production would not remain elevated.[10] Trophic interactions can also take time to result in a community-level response. For example, after the elimination of three species of seed eating rodents from a desert plant community studied by Brown and Heske,[11] it took 12 years for the plant community to shift to grasses, an interval greater than predicted by the investigators. Thus, our conclusions about the effect of a perturbation may depend upon the time scales of the ecosystem responses and the time scales of our observations of the ecosystem. Analogous to the terrestrial FACE experiments are the FOCE (free-ocean carbon dioxide enrichment) experiments (http://www.mbari.org/mars/science/foce.html), which should help reveal the temporal patterns of in situ responses of species to OA.

These three key observations are just a part of the guidance provided by previous ecological study of environmental change. As we continue our multiagency endeavors to study OA, our efforts need to (1) be informed by previous large-scale study of environmental change impacts and (2) have a framework that both guides the research and allows us to assess if we are addressing all key areas.

■ A RESEARCH FRAMEWORK

We propose a framework for continued study of OA that would span key questions ranging from seawater carbon chemistry to ecosystem response. We structured our framework in a triangular diagram that reflects the connectedness of different levels of study (Figure 1). First, there is still uncertainty surrounding the impacts of projected climate and ocean circulation changes on the physical and chemical processes that govern the ocean's capacity to absorb CO_2, an interplay represented by the arrow labeled (1) in Figure 1. Then, changes in seawater carbon chemistry differentially affect individual organisms, populations of species, and ecosystems, often through changes to biogeochemical processes. Because effects on individual species (Arrow 2), when added together, can be nonlinear and influenced indirectly, system-level phenomena do not necessarily reflect the sum of their components (Arrows 3 and 4). Finally, we recognize that ecosystems and the carbon cycle can interact and result in an intricate feedback loop (Arrows 5 and 6).

For each labeled arrow or set of arrows, we outline the central question and key testable hypotheses (Table 1). We focus on several general and tractable hypotheses for each Arrow, and recognize that our list is not exhaustive. Arrow 1 represents a link between the atmosphere and seawater and focuses on biogeochemical hypotheses that provide the basis for more ecological hypotheses represented by Arrows 2 through 6. We also recognize that our expectations will differ in coastal versus open ocean environments. Finally, we ask how funded research projects in the U.S. cover this conceptual framework by reviewing where OA funding is being directed among these 6 arrows.

(Arrow 1) How Will the Partitioning of CO_2 between the Ocean and the Atmosphere Change with Increasing Anthropogenic CO_2? Arrow 1 is represented in green because we have a solid understanding of the basic processes responsible for the feedback between atmospheric and seawater CO_2. The effects of anthropogenic CO_2 on ocean chemistry are relatively well understood due to research motivated—in part—by the related climate change issue of oceanic and atmospheric warming. The oceans have absorbed approximately one-third of all anthropogenic CO_2,[12,13] and continue to absorb approximately one-quarter of all modern emissions.[14,15] The decrease in the uptake fraction is primarily attributable to changes in ocean chemistry. Marine uptake of anthropogenic carbon increases dissolved seawater CO_2 concentrations and drives the conversion of carbonate (CO_3^{2-}) to bicarbonate (HCO_3^-) through the net reaction:

$$CO_2 + H_2O + CO_3^{2-} \leftrightarrow 2HCO_3^- \qquad (1)$$

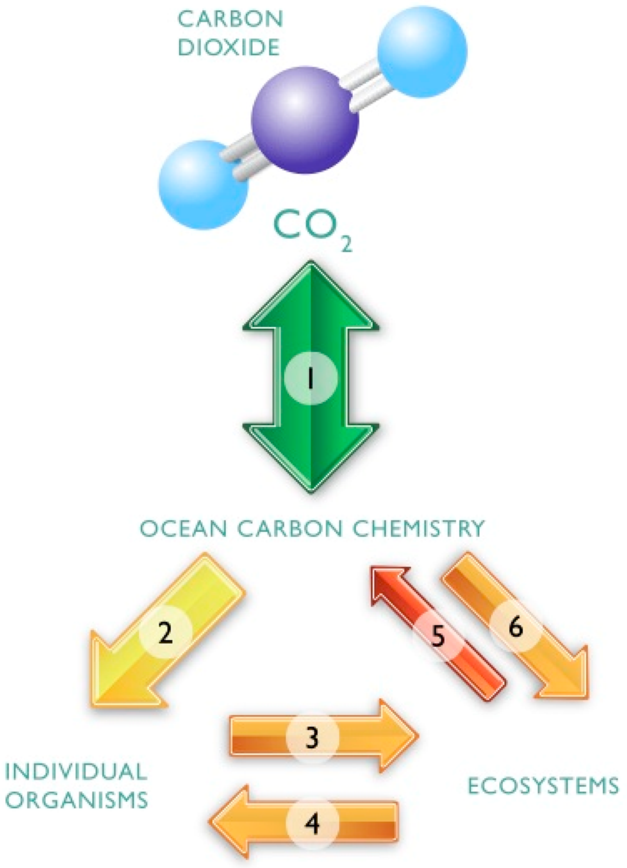

Figure 1. A framework for the study of Ocean Acidification. Each key linkage (or Arrow) is denoted with a number between 1 and 6, corresponding to a set of hypotheses presented in the text. The framework is divided into "C" for Coastal Ocean and "O" for Open Ocean. We color-coded the arrows to indicate green for a well-understood linkage and yellow for strong current research programs, while orange indicates nascent understanding in the area and red indicates a dearth of data for the linkage. We quantified the extent of current research in the U.S. associated with each arrow by tallying the studies presented in posters at the Ocean Acidification Principal Investigator's (OAPI) meeting in September 2013 (72 posters) and the U.S. National Science Foundation OA grants awarded in 2013 (n = 13), (Table 2). Our tallies slightly exceed 100% because two studies encompassed two linkages.

Another key reaction occurs increasingly as carbonate ions are depleted in seawater:

$$CO_2 + H_2O \leftrightarrow H^+ + HCO_3^- \qquad (2)$$

Reaction 2 increases seawater hydrogen ion concentrations and gives ocean acidification its name. Hydrographic surveys have measured changes in marine carbon chemistry resulting from CO_2 uptake with decadal resolution,[3,16−18] while a handful of time series have made measurements at higher frequencies.[19−23] Our comparatively solid understanding of the role of CO_2 in ocean chemistry has allowed for future projections of anthropogenic changes to the oceans, although many projections focus on surface ocean pCO_2 and all rely upon uncertain predictions of future anthropogenic carbon releases.[12,24−26]

Future research relating to Arrow 1 should address the comparatively poorly understood processes acting on ∼100 years to millenial time scales (lagged responses), emergent properties of the climate system that arise due to interactions between OA and other aspects of climate change, and nonlinear feedbacks between biological responses to OA and atmospheric CO_2. As with the observations for increases in CO_2 in terrestrial systems, lagged responses are expected. Because large temporal and spatial scales involved, we suggest that hypotheses are tested using simulations from computer models constructed with the best available knowledge of OA feedbacks will be a valuable tool for Arrow 1.

Hypothesis 1a: On Time Scales of Centuries and Longer, Ocean Acidification Will Alter the Distribution of Carbon between the Atmosphere, The Upper Ocean, And the Deep Ocean. The export of biological organic matter removes carbon from the surface ocean and results in net oceanic uptake of carbon from the atmosphere, while carbonate mineral precipitation leads to a loss of carbon from the ocean to the atmosphere.[27,28] If OA results in increased organic matter formation due to increased CO_2 or inhibition of carbonate mineral cycling through decreased CO_3^{2-}, then OA will also shift the balance between these processes and thus the partitioning of carbon between the ocean and the atmosphere.[29−32]

Hypothesis 1b: Changes to Physical Processes Such As Eddy Dynamics Will Change the Partitioning of Carbon between the Ocean and Atmosphere over the Next 100 Years. Changes in atmospheric heat budgets are projected to continue to perturb wind patterns, especially over the Southern Ocean, and this may alter the natural eddy field. While the imprint of mesoscale eddies on local climate and biology has been studied,[33] it remains unclear to what degree broad scale changes in eddy dynamics (e.g., a structure) will affect natural biogeochemical cycling (e.g., a function).

Hypothesis 1c: An Intensified Hydrological Cycle Will Perturb the Historic Distribution of Freshwater Inputs to the Ocean, Thus Impacting Its Buffering Capacity. Changes in pH resulting from CO_2 uptake are buffered by seawater alkalinity. Because seawater alkalinity is linearly diluted by freshwater, and we expect regional shifts in patterns of evaporation, precipitation, sea ice cycling, riverine runoff, and glacial icemelt,[34] it follows that we should anticipate regional OA sensitivity changes.

Hypothesis 1d: Over Time Scales of Millennia and Longer, A Carbon Pulse from Dissolution of Sediment Minerals Will Further Alter the Chemistry of Seawater. "Carbonate compensation" refers to the dissolution of carbonate minerals stored as seafloor sediments[35−38] and terrestrial carbonates[39,40] in response to decreases in ocean pH. Carbonate dissolution increases seawater alkalinity, pH, and CO_2 solubility, while acting as a negative feedback to changes in atmospheric CO_2. Sedimentary carbonate dissolution is proportional to both the saturation state of overlying seawater and the amount of CO_2 released within sediments through organic matter remineralization.[36,41] OA will lower the seawater−carbonate saturation state above sediments and has the potential to alter the ratio between organic matter and carbonate mineral export to deep sea sediments. OA will therefore likely enhance sedimentary carbonate dissolution and increase ocean alkalinity and carbon storage as a lagged ∼10 000+ year response to OA.[27]

Hypothesis 1e: The CO_2 Dynamics of an Organism's Environment Will Be Regionally Specific, And Subject to Other Anthropogenic Stressors. Recent attention has focused on the coastal oceans and marginal seas where carbon

Table 1. Summary of the Hypotheses Associated with Each Arrow Based on the Framework Provided in Figure 1, Each Hypothesis Is Discussed in Greater Detail in the Text

Arrow 1) How will the partitioning of CO_2 between the ocean and the atmosphere change with increasing anthropogenic CO_2?
Hypothesis 1a: On timescales of centuries and longer, ocean acidification will alter the distribution of carbon between the atmosphere and the deep ocean.
Hypothesis 1b: Changes to physical processes such as eddy dynamics will change the partitioning of carbon between ocean and the atmosphere over the next 100 years.
Hypothesis 1c: An intensified hydrological cycle and changes to freshwater inputs will impact ocean buffering capacity.
Hypothesis 1d: Over timescales of millennia and longer, a carbon pulse from dissolution of sediment minerals will further alter the chemistry of seawater.
Hypothesis 1e: The CO_2 dynamics of an organism's environment will be regionally specific, and subject to other anthropogenic stressors.
Arrow 2) Are elevated CO_2 levels detrimental to marine organisms?
Hypothesis 2a: Species will differ in fitness-conferring traits affected by ocean acidification.
Hypothesis 2b: Life stages are differentially susceptible to ocean acidification.
Hypothesis 2c: Species will differ in their adaptive capacity to ocean acidification.
Hypothesis 2d: In addition to carbon chemistry changes, species will experience increases to other stressors where Hypotheses 2a, b, c above may also apply.
Arrow 3) Does OA affect organisms differentially to influence ecosystem properties?
Hypothesis 3a: If OA affects those species with strong interactions in the system, then we expect an ecosystem response in terms of function (e.g. productivity or resilience)
Hypothesis 3b: If OA affects those species with strong interactions in the system, then we expect an ecosystem response in terms of structure (e.g. taxonomic diversity)
Hypothesis 3c: If OA increases fitness of one or a few species with particular traits, then we expect an ecosystem response.
Arrow 4) Does OA change ecosystem level properties that feedback to individual species?
Hypothesis 4a: The effects of OA on a species may be mediated via biotic interactions or by abiotic conditions.
Hypothesis 4b: The effects of OA on ecosystems may establish pathways for novel indirect effects.
Arrow 5) Does ecosystem response affect carbon chemistry?
Hypothesis 5a: High primary production results in higher saturation states and decreased pCO_2
Hypothesis 5b: Changes in diversity and abundance of animals and phototrophs will alter carbon cycling
Hypothesis 5c: Changes in higher trophic level abundance (e.g. fishes) alter the cycling of carbon
Hypothesis 5d: Seasonality in species metabolism (e.g. remineralization) will impose higher variability in carbon cycling in coastal areas.
Arrow 6) *Does OA affect ecosystem response?*
Hypothesis 6a: OA will affect the structure of an ecosystem via an effect on carbon cycling
Hypothesis 6b: OA will affect the function of an ecosystem an effect on carbon cycling

chemistry can vary spatially[42] and temporally.[4,43] Our understanding of the expected changes to nearshore chemistry is less constrained compared to the open ocean. The added complications of this variability may lead to uncertainty in predicting the response of organisms to OA in coastal or otherwise variable regions.

In addition to the natural variability, there are other related changes to the biogeochemistry of the oceans due to climate change such as oxygen depletion, temperature increases, and changes to freshwater and nutrient inputs and cycling. These effects may be either direct or indirect and may alter the partitioning of carbon between the ocean and the atmosphere providing further feedbacks to OA. Anthropogenic nutrient loading enhances eutrophication and the same respiratory processes that lead to local hypoxia produce additional CO_2. In fact, pH changes since the onset of the industrial revolution in the eutrophication zones in the northern Gulf of Mexico are greater than would be expected solely on atmospheric CO_2.[44]

(Arrow 2) Are Elevated CO_2 Levels Detrimental to Marine Organisms? To date, the majority of effort directed at understanding the biological implications of OA has focused on individual organisms, mainly calcifying invertebrates and phototrophs (Figure 1), and there are several excellent reviews discussing this subject.[45−53] We extend this review material by focusing on four general hypotheses to enhance future research efforts.

Hypothesis 2a: Species Will Differ in Fitness-Conferring Traits Affected by Ocean Acidification. When assessing the long-term impacts of OA on marine organisms, it is important to identify the traits that most dramatically affect the fitness of a species. Fertilization success is a trait of particular importance to broadcast spawning invertebrate species[54] and shows a diversity of response to OA, including some species with remarkable sensitivity[55−58] and others with no apparent effects.[59−61] To date, we have relatively little understanding of reproductive success in more mobile species, although elevated pCO_2 levels stimulated the reproductive output in the anemone fish, *Amphiprion melanopus*,[62] while having no impact on two copepod species.[63] Particularly for longer-lived species, however, reproductive consequences of OA over the entire life cycle remain untested and therefore unknown.

Traits that alter the cost of OA to organisms will be indirectly tied to fitness by affecting resources that could otherwise be dedicated to reproduction and survival. A nonexhaustive list includes impacts on growth,[64−66] metabolic rate,[67−69] photosynthesis,[70,71] calcification and the formation of key noncalcified materials,[53,72−76] tissue health,[77] and underlying physiological pathways.[78−81] Additionally, a suite of behavioral effects has been documented with respect to olfactory and auditory sensing,[82,83] learning,[84] as well as compromised predator−prey detections,[85−88] all with serious consequences at both the individual and ecosystem level.[89] A common point between these impacts of OA is that responses are rarely uniform across organisms−even between closely related species,[90] setting the stage for shifts in relative species abundance in the oceans. Research efforts that hone in on those traits that make a species sensitive or tolerant to OA should remain a priority.

Hypothesis 2b: Life Stages Are Differentially Susceptible to Ocean Acidification. Early life stages of organisms are typically the most sensitive to environmental perturbations, which is likely also true for OA. In fact, there have been reports of reduced larval survival in fish,[91] urchins,[92] crabs,[93] and bivalves[94−96] in response to OA, although these effects are not ubiquitous.[97] Interestingly, porcelain crabs appear to be more sensitive as juveniles than larvae,[98] emphasizing the need to understand the ontogenetic factors that define the survival thresholds for pCO_2 exposure.

Sublethal end points are also important for larval organisms in an ecological context owing to important early life environmental transitions. For example, many planktonic larvae transition to benthic habitat where they subsequently join adult populations. This recruitment period can be associated with high mortality rates and OA has been found to exacerbate this mortality in two very important ways. First, OA has been shown to inhibit olfactory capabilities of larval fish, reducing their ability to identify suitable recruitment habitat and potential predators in reef fish species.[82,85,89] These factors alone are anticipated to substantially impact the long-term health of reef fish populations,[89,99] and future work should examine impacts on other recruitment cues (e.g., auditory) and habitats (e.g., seagrass). Second, predator-based mortality during recruitment may also be further influenced by reduced growth of OA exposed individuals. It is well established that rapid growth of larval cohorts reduces vulnerability to predators by allowing individuals to more quickly reach established size-escape thresholds.[100] By inhibiting larval growth, OA will likely extend the vulnerability window of many marine larvae.[91,99]

Hypothesis 2c: Species Will Differ in Their Adaptive Capacity to Ocean Acidification. Understanding the ability of marine organisms to adapt to predicted environmental change is a crucial aspect of OA research. What species are resilient? Do species possess the capacity to adapt to a changing ocean and does this ability differ among species? When assessing these questions for OA, much can be learned from research efforts to understand global warming, which has highlighted three important areas when considering adaptive capacity: (1) evolutionary genetic change, (2) phenotypic plasticity, and (3) transgenerational plasticity.

Recent theories discussing evolutionary rescue provide guidance for the role genetic processes may play in species resilience to OA.[101,102] These theories address responses to deteriorating environments and emphasize the importance of existing genetic variation within a population that may harbor successful heritable genotypes. This may be especially true for those species living in regions of upwelling, highly variable, or otherwise extreme environments that already experience periods of high-CO_2 exposure. In addition, species with short generation times (e.g., coccolithophores) may respond to environmental alterations through adaptive evolution.[103]

The importance of genetic variation in species has been demonstrated recently both with respect to genome-wide analysis[104] and specific fitness-conferring traits.[105,106] However, our overall understanding of the scope for adaptation remains limited to relatively few species. A second important characteristic for evolutionary rescue is overall population size. Small populations are more at risk because they lack the overall scope for standing resilient genotypes.[107] This is a particularly important point when considering OA and conservation strategies for harvested species.[52]

Phenotypic plasticity refers to the ability of organisms to alter their phenotype in response to environmental variables and thereby buffer against detrimental impacts of environmental variation. Physiological plasticity could play a key role for OA given the importance of acid−base homeostasis.[78,79,108] In fact, comparative physiologists have long been interested in the dynamic responses of organisms to changing environments, and much can be learned from these studies with respect to experimental approaches. A common approach is to identify distinct populations of a species that are exposed to different environments, which has been used effectively by examining species native to naturally high-CO_2 areas.[104,105] A second common approach is to monitor an organism's response to environmental change through time,[78,109] often highlighting transcriptional, translational or morphological responses; however, it is important to anchor transcriptional changes to phenotype.

Transgenerational plasticity (TGP), whereby adults exposed to OA confer advantageous traits to offspring through epigenetic mechanisms, may also have implications for OA.[110,111] TGP is particularly prevalent in species coping with rapid environmental change.[112,113] The current evidence for TGP suggests that some species are already adapted to rapid changes in pH and pCO_2 levels, as it is a characteristic feature of many coastal habitats, and these lab studies have recently been extended to field studies demonstrating seasonal changes in pCO_2 sensitivity in Atlantic silversides (*Menidia menidia*).[114] Unlike the open ocean, future pCO_2 levels in coastal environments may be difficult to predict; and consequently it is not known whether short-term adaptations to high CO_2 via TGP may translate into long-term resilience of these species. A final consideration is the recognition that adaptive responses, via plasticity, TGP or other means, may also come with fitness costs by inducing trade-offs.

Hypothesis 2d: In Addition to Carbon Chemistry Changes, Species Will Experience Increases to Other Stressors Where Hypotheses 2a, b, c above May Also Apply. Ocean acidification is only one of many components of global change and, as pointed out in several reviews,[50,115] it is important that moving forward, researchers consider multiple stressors. The most obvious overlapping global climate change is the predicted increase in sea surface temperature associated with global warming, an interaction that is being increasingly explored with experiments.[116] Increasing sea surface temperatures are not only another significant stressor, but temperature has a direct effect on seawater carbonate chemistry. Important additional stressors include altered freshwater inputs into the marine environment, both through changing hydrological factors (*Hypothesis 1c*) and anthropogenic influences, as well as changing occurrence and duration of marine hypoxia events. Importantly, in many marine habitats hypoxia and high CO_2 occur concurrently with potential neutral, additive and/or synergistic effects of these two stressors.[117,118]

Coastal ecosystems are of particular interest with respect to multistressor studies as these environments are in some cases already subject to dramatic shifts in salinity, temperature, and nutrient input, as well as daily fluctuations in oxygen and carbon dioxide. Furthermore, the coastal environment is particularly at risk from harmful anthropogenic inputs stemming from agriculture or urban runoff leading to eutrophication and polluted environments, respectively. On the one hand, because species in coastal areas typically experience high environmental variation, they may act as a reservoir for population and species resiliency; alternatively, persistent exposure to multiple stressors may increase their susceptibility to increasing OA.

As OA studies continue, it is essential that our inference is a result of from well-designed and replicated experiments. The EPOCA guide for OA addresses some essentials,[119] but we note that there are other important considerations. First, taxonomic representation needs to be broad. Further, the scope for adaptation may depend upon the variability that organisms experience; natural fluctuations in pH are beginning to be included in experimental manipulations of pH.[65,117] Finally, in order to understand the functional relationship between pH changes and organism response, our experiments need to move beyond a simple treatment and control comparison to one where a number of treatment levels, including increasing levels of pCO_2 and interactions with other stressors, to understand the functional response of organisms.

(Arrow 3) Does OA's Differential Effect on Organisms Influence Ecosystem Properties? We expect differences in sensitivity among species to ocean acidification and it is these differences that will likely drive changes to the structure and function of an ecosystem. Ecosystem changes may include altered taxonomic and functional diversity, energy flow, ecosystem resilience, and structural complexity. Empirically, an investigator interested in quantifying an ecosystem response might thus measure overall carbon fixation, community calcification, nutrient sequestration or loss, or a metric of variability in multispecies abundance. Possible changes in ecosystem structure and function in response to OA are indicated by in situ studies along natural gradients in pH, pCO_2, or saturation state. Shallow, submarine CO_2 seep sites from the Mediterranean Sea, a tropical reef in Japan, and coral reefs in Papua New Guinea have provided sites to perform mensurative experiments with multiple species and functional responses, including diversity changes. Though these ecosystems are an informative addition to controlled laboratory conditions and provide a proxy for ocean acidification impacts at the ecosystem level, there are recognized limitations of present-day CO_2 seep sites. Extrapolations from seeps have limitations, because pCO_2 is often more variable at seeping locations than in surrounding regions,[120] and because seeps are comprised of open populations.

Hypothesis 3a: If OA Affects Those Species with Strong Interactions in the System, Then We Expect an Ecosystem Response in Terms of Structure (e.g., Taxonomic Diversity). Reductions in taxonomic diversity are often predicted with ocean acidification. If species losses include those species with strong interactions in the system, including keystone, engineer, or foundational species, then we expect effects to reverberate throughout the system. For example, at shallow volcanic CO_2 seeps in Papua New Guinea, pH declines from 8.1 to 7.8 without a corresponding temperature change. Increases in CO_2 corresponded with reductions in hard coral species richness, including increased coverage of massive *Porites* and loss of diversity from structurally complex corals (e.g., branching, foliose and tabulate growth forms).[121] The implication for losses in hard and structurally complex corals could be a decline in habitat availability and quality for juvenile fish and many invertebrates. Even if the losses represent only local extirpations, local diversity reduction may still be significant. CO_2 seeps at subtidal temperate sites in the Mediterranean off the coast of Ischia also exhibited reductions in taxonomic diversity with pH declines.[5] Scleractinian corals were absent from high venting regions, and reductions in sea urchin and coralline algal abundances were significant. Following disturbance events (clearing of benthic plots) at this site, recovery patterns of rocky benthos were less variable than at ambient pH sites, resulting in homogenization and reduced functional diversity at pH levels reflective of near-future and extreme scenarios for ocean acidification.[122,123] The biofilms and filamentous algae that rapidly recolonized the cleared plots at reduced pH remained abundant throughout recovery. OA effects on a species that strongly interacts in a system may in turn affect the abundance of other species, an outcome suggested in a guild of coralline algae at a site in the northeast Pacific where pH is in decline. A former competitively dominant alga has declined in thickness since the 1980s[124] and now loses approximately half of its competitive bouts, an effect that has resulted in greater intransitivity of competitive outcomes in the system.[125] These relatively recent examples highlight in situ observations of alterations in ecosystem taxonomic and functional diversity resulting from differential sensitivity of species to reduced pH.

Hypothesis 3b: If OA Affects Those Species with Strong Interactions in the System, Then We Expect an Ecosystem Response in Terms of Function (e.g., Productivity or Resilience). Many primary producers are expected to benefit from ocean acidification, leading to an increase in ecosystem productivity. At CO_2 vents off Ischia and Papua New Guinea, seagrass cover increased with decreasing environmental pH.[5,121] Shoot densities, but not below-ground biomass, were three to four times higher at >500 ppm pCO_2. Increased seagrass and macroalgal cover corresponded with reductions in epiphytes in both vent regions.[121,126]

Loss of structure-forming species, such as structurally complex corals, to ocean acidification (perhaps exacerbated by seawater temperature increases) indirectly affects macroinvertebrate groups through loss of habitat and refugia.[127] At high-CO_2 seep sites in Papua New Guinea, total density and representative phyla of macroinvertebrates was reduced to 48% and 85% of control values, respectively, and was associated with a reduction in reef structural complexity. Densities of those taxa that were strongly reduced at high CO_2 were mobile groups, while densities of sessile taxa were unaltered.

The demonstrated keystone status of calcifying species such as the seastar, *Pisaster ochraceous*, and the sea urchin, *Strongylocentrotus purpuratus*, in the northeast Pacific suggest that calcifying species such as these may initiate structural and functional changes to ecosystems. Similarly, taxa that respond to environmental change and have a central trophic position, will likely influence community structure through range changes and biotic interactions.

Hypothesis 3c: If OA Increases Fitness of One or a Few Species with Particular Traits, Then We Expect an Ecosystem Response. Even if species affected by OA are not, by themselves, strong interactors in the ecosystem, shared traits among species may lead to an ecosystem response. For example, OA may change the diversity of ecological systems, based on evidence from CO_2 vent communities where sites with decreased pH show a shift to a species-poor community dominated by fleshy algae.[128] Mesocosm experiments where pCO_2 is manipulated also suggest a decreased diversity of macroalgae with increased pCO_2.[129] Given the demonstrated linkages between species diversity and ecosystem function,[6,130] OA can be a stressor that stimulates a negative feedback loop where diversity erodes and a functional change occurs.

(Arrow 4) Does OA Change Ecosystem Level Properties That Feedback to Individual Species? The effects of ocean acidification on individual species could also occur via indirect pathways, in which the direct effects of high CO_2 alter components of the ecosystem that inhibit those taxa not directly at risk from high CO_2. Again, many insights into indirect effects of ocean acidification are derived from in situ studies conducted along strong gradients in pCO_2, and from mesocosm experiments that allow controlled tests of ecological interactions.

Hypothesis 4a: The Effects of OA on a Species May Be Mediated via Biotic Interactions or by Abiotic Conditions. Indirect effects of high CO_2 can be driven via biotic interactions if changes in the producer or consumer component of the ecosystem inhibit or facilitate other taxa via resource availability or competitive interaction. As an example, mat-forming algae in temperate kelp forests and tropical coral reefs are hypothesized to have enhanced productivity with increased CO_2 resources,[131,132] perhaps outcompeting kelps and corals. Hence both kelps and corals, in their respective habitats, may be indirectly inhibited by high CO_2 via space-holding competitors that are released from carbon limitation. Shifts in the competitive dominants of each respective ecosystem may result.[133] Another indirect pathway by which kelp and coral are further inhibited is by the negative effects of mat-forming algae on coral and kelp recruitment.[134,135] We note, however, that if OA has deleterious effects on their grazers, algae may experience a net benefit.

Changes in resources could also lead to indirect effects on consumers via changes to the quantity and quality of their food source.[136] For example, when turf algae and their herbivores were grown in high-CO_2 concentrations, the algae had increased nitrogen content. Per capita herbivory rates of gastropods, in turn, increased, suggesting elevated energetic needs under OA.[137] Similarly, negative effects of increased CO_2 on pteropods and the diverse assemblage of zooplankton may have indirect effects on the fishes that feed on them.[138] If decreases in pteropods result from their inability to calcify and maintain shells under high-CO_2 conditions, then food webs in high latitude regions will be affected, as well as the substantial export flux of carbon and carbonate. A further consideration is the outcome if a species susceptible to OA is a member of a higher trophic level. The possibility of trophic cascades, or the alternate control of competitive versus consumers across all trophic levels, is a likely outcome if a top predator is affected by OA.

Hypothesis 4b: The Effects of OA on Ecosystems May Establish Pathways for Novel Indirect Effects. Because OA likely affects biogenic structures that provide habitat to many species (e.g., corals), any dissolution of these structures or susceptibility to disturbance will indirectly affect many species. For example, the snail *Littorina littorea* fails to induce shell defenses under decreased seawater pH, a response that affects its crab predators.[139]

(Arrow 5) Does Ecosystem Response Affect Carbon Chemistry? We generally think about the effects that changing environments can have on organisms and ecosystems, but ecosystems can also have both positive and negative feedback on the environment. Changes in community diversity, structure, and abundance can all alter carbon cycling via biogeochemical reactions that impact the carbon cycle including photosynthesis, respiration, and calcification. We highlight key examples below where ecosystem responses can affect ocean carbon chemistry.

Hypothesis 5a: High Primary Production Results in Higher Saturation States and Decreased pCO_2. Primary producers utilize CO_2 through photosynthesis, which decreases pCO_2 and ultimately increases pH and $CaCO_3$ saturation state. A 10-year time series of pH data from a rocky intertidal zone in the Eastern Pacific off of Washington State showed typical diel fluctuations of about 0.24 units, reflecting net photosynthesis during the day and net respiration at night.[4,20] A subtidal macrophyte meadow in the Baltic Sea, characterized by brown algae and seagrass, showed mean diel pH variability of 0.34 units during the month of August.[140] Additionally, a multi-ecosystem comparison found semidiurnal and diel pH variability patterns at different coastal locations categorized as upwelling, estuarine/near-shore, coral reef, kelp forest, and extreme.[42] Over a 30 day period, diel pH fluctuations were 1−2 orders of magnitude larger at tropical and temperate coastal locations (0.121−1.430 units) compared to open-ocean and polar locations (0.047−0.096 units) [42]. In sum, how phototrophs affect pCO_2 and $CaCO_3$ saturation state varies regionally and has been greatest in coastal locales.

Hypothesis 5b: Changes in Diversity and Abundance of Phototrophs and Heterotrophs Will Alter Carbon Cycling. The diversity of both heterotrophs and phototrophs is expected to decrease as ocean pH decreases as predicted by mesocosm manipulations and studies near natural vents.[121,122,141] Loss of biodiversity could impact carbon and nutrient cycling. In grassland ecosystems, increased diversity led to increased productivity and nutrient utilization.[6] If applied to an OA scenario, we hypothesize that decreased diversity in marine phototrophs could reduce productivity and result in incomplete nutrient utilization, leading to less fixed carbon and lower chlorophyll/nutrient ratios. Reduced primary production by phototrophs in surface waters would limit resources available for heterotrophs and would reduce carbon export out of the euphotic zone, altering global carbon cycles and nutrient utilization and potentially leading to positive feedback for the carbon content of the surface ocean.

Changes in community structure as a result of OA could impact carbon chemistry in various ways, depending on how the community structure changes. For example, in macroalgal communities, fleshy turf-forming algae may have a competitive advantage over kelp and calcareous species with increasing OA.[142,143] Different macroalgal species have different growth rates and utilize carbon and other nutrients at different rates, thereby changing carbon chemistry dynamics. With regard to heterotrophs, calcifying animals are expected to fare poorly under high pCO_2 conditions compared to noncalcifying animals. While all animals produce CO_2 through respiration, calcifying animals also produce one mole of CO_2 for every mole of $CaCO_3$ produced (eq 3).

$$Ca^{2+} + 2HCO_3^- \leftrightarrow CaCO_3 + CO_2 + H_2O \tag{3}$$

This production of CO_2 further reduces pH and also reduces alkalinity. Therefore, a shift away from calcifying species could impact carbon chemistry and may partially offset OA. Furthermore, in planktonic species such as pteropods, and coccolithophores $CaCO_3$ acts as ballast and facilitates the transport of organic carbon to the deep ocean.[144,145] If the abundance of such species decreases, there could be impacts on the ocean carbon pump. The abundance of heterotrophs and phototrophs is inherently linked through consumer-resource interactions such that changes in the dominant species of each group could result in imbalances. In general, if the balance shifts toward phototrophs, there could be net primary production, utilizing CO_2 and increasing pH. If the balance shifts toward animals (heterotrophs), there would be net respiration, increasing production of CO_2 and decreasing pH.

Hypothesis 5c: Changes in Higher Trophic Level Abundance (e.g., Fishes) Alter the Cycling of Carbon. Organisms occupying higher trophic levels, such as fish, also impact carbon cycling in the ocean. The importance of the role that fish play in the inorganic carbon cycle has only recently come to light.[146,147] High magnesium calcite, a form of $CaCO_3$ more soluble than aragonite, is produced in fish intestines as a byproduct of osmoregulation, as fish constantly drink seawater. The high-Mg calcite is excreted in mucus-coated pellets.[148] This fish intestine calcification could account for 2.7−15.4% of the estimated total new $CaCO_3$ production in surface oceans,[146] making it a significant portion of surface ocean $CaCO_3$ production. The production of the $CaCO_3$ pellets lowers alkalinity where they are produced. In shallow regions, where the pellets do not dissolve before sinking to the seafloor, their production will lower alkalinity. It has been estimated that fish contribute an average of 14% to the total estimated carbonate mud production across the Bahamian archipelago.[147] Furthermore, fish also produce H^+ ions, which they excrete into seawater through their gills.,[149] decreasing both pH and alkalinity. If fish biomass changes with OA, as indicated by overharvesting in many marine ecosystems,[130] the production of $CaCO_3$ and H^+ ions by fish will also change correspondingly, altering carbon cycling.

Hypothesis 5d: Seasonality in Species Metabolism (e.g., Remineralization) Will Impose Higher Variability in Carbon Cycling in Coastal Areas. In addition to the effects of primary producers, coastal and estuarine systems are subject to carbon chemistry conditions that vary on daily and greater time scales. Additionally, coastal and estuarine systems are potentially more susceptible to OA than open oceans.[34,150,151] As these regions become eutrophic (excessive nutrient levels that lead to algal blooms), bottom waters become hypoxic or anoxic due to microbial consumption of organic matter.[152] Microbial consumption is coincident with the metabolic production of CO_2, which further reduces pH. During respiration (or remineralization), as oxygen is used up, CO_2 is produced, lowering pH. This process is generally seasonal, as the algal blooms start in spring when the water column stratifies and there is more light available, resulting in seasonally variable carbon chemistry.

(Arrow 6) Does OA Affect Ecosystem Response? Here we incorporate instances where an *ecosystem response* variable was assayed following an OA perturbation. In contrast, Arrows 2 and 3 represent the direct link between ocean carbon chemistry and an individual species (Arrow 2). A study that focused on the calcification of a particular coral species, for example, would be placed in Arrow 2, while a study that measured reef-wide calcification rate would be in Arrow 6. If OA negatively affected a single dominant species with overall fish species diversity declining, Arrow 3 would represent that process.

Increased carbon dioxide pollution, as with anthropogenic nitrogen pollution, provides a resource subsidy to some member of the system, a subsidy that can become a stress as levels increase.[153] We thus expect changes to the carbon cycle through an increase in carbon or a relative change in the availability in the type of dissolved inorganic carbon to result in a change to the structure or function of an ecosystem.

Hypothesis 6a: OA Will Affect the Structure of an Ecosystem via an Effect on Carbon Cycling. Structural changes in an ecosystem might result from OA independent of whether single species changes have cascading or competitive effects. For example, if increased pCO_2 stimulated carbon fixation and growth of all producers relative to consumers, a structural effect on the distribution of biomass across trophic levels would result. Similarly, structural changes are expected in ecosystems due to the negative effect of OA on calcifying species, a taxonomically diverse group. Species composition might shift while diversity does not change, as suggested by a relative dominance of picoplankton at the expense of diatoms when CO_2 and inorganic nutrients were increased in the Svalbard mesocosm experiments.[154]

Hypothesis 6b: OA Will Affect the Function of an Ecosystem via an Effect on Carbon Cycling. Functional ecosystem responses resulting from a direct effect of OA, presumably via the provision of greater CO_2 and HCO_3^-, are supported in experiments where carbon uptake and primary production increase with increasing pCO_2.[154] Although enhanced primary productivity and thus decreased pCO_2 might be thought of as a positive effect on an ecosystem service, whether nutrient limitation will inhibit the long-term carbon response, as in the Progressive Nutrient Limitation Hypothesis posited for terrestrial systems, remains to be studied. Increasing pCO_2 has been shown to increase growth of some turf algal species and phytoplankton.,[152] while kelp species did not show this response.[142] A productivity response by phototrophs may be most likely in areas where nitrogen is increased due to anthropogenic inputs. Thus, our understanding of OA effects on ecosystem function through changes in productivity is dependent on the availability of nutrients other than carbon, as well as phototroph physiology and interactions. Combined with our discussion of Hypothesis 5a, it becomes clear that some structural and functional responses to OA will likely involve feedbacks. For example, a stimulation of primary production by increased pCO_2 could result in greater diel and seasonal variation in pH as some producers drive up pH, making carbon less accessible to other producers.

A Summary of Research Coverage to Date. Finally, we ask how ongoing research programs in the U.S. have covered this conceptual framework that spans carbon chemistry and individuals to ecosystems (Figure 1). To quantify the coverage, we used two sources of information: (1) the content of posters presented at the OA Principal Investigators Meeting in September 2013 in Washington, DC and (2) the most recent proposals funded by the NSF Ocean Acidification panel in July 2013. These two sources should integrate and be representative of the recent research efforts funded by the NSF and NOAA, as the meeting was mandatory for those receiving federal funds to do OA research and any new awardees were included in the July 2013 announcement. In total, there were 72 studies where the research content could be assigned; 15 others were excluded because they dealt with outreach or meeting summaries. We find that much of the current research is focused on understanding the interplay between the atmosphere and seawater, as well as the effects on single species (Table 2). There have also been efforts (14.3%) to understand the effects of OA on ecosystem-level responses (Arrow 6), and these have been focused in coastal systems.

We found few funded research efforts to link individual responses to system-level responses, though we acknowledge that there is ongoing research with mesocosms and at CO_2 vent sites that were not encompassed in these recent U.S. funding efforts. Thus, the scientific community has relatively little predictive power to understand how the results of scaled-down bottle and mesocosm studies will scale-up to the ecosystem level and whether emergent properties will occur (e.g., Arrow 3). Further, there was no apparent effort focusing on how system-level biological changes will feed back to ocean carbon

Table 2. We Quantified the Extent of Current Research in the US Associated with Each of the Six Main Linkages Described in Figure 1 by Tallying the Studies Presented in Posters at the Ocean Acidification Principal Investigator's (OAPI) Meeting in September 2013 (72 posters) and the U.S. National Science Foundation OA Grants Awarded in 2013 (n = 13)[a]

linkage number	linkage type	% coastal studies	% open ocean studies
1	CO_2 to ocean carbon chemistry	14.3	11.4
2	ocean carbon chemistry to individual organisms	47.0	10.0
3	individual organisms to ecosystems	1.4	0
4	ecosystems to individual organisms	0	0
5	ecosystems to ocean carbon chemistry	1.4	0
6	ocean carbon chemistry to ecosystems	14.3	1.4

[a] Our tallies slightly exceed 100% because two studies encompassed two linkages. We split these studies into groups that focused either on Coastal or Open Ocean areas.

chemistry (Arrow 5). Given that biological processes such as carbon fixation, respiration and nutrient uptake have been associated with driving substantial diel variability in coastal carbon cycles,[4,43,155] and that marine phototroph composition is predicted to change,[142,156] it is feasible that the link between system-level properties and ocean carbon (Arrow 5) could be significant.

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Notes

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