Modeling changes in ocean biogoechemistry due to climate change and ocean acidification

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As rising anthropogenic carbon dioxide emissions have contributed to climate change by altering the Earth's radiative balance, about one-third of this carbon dioxide (Sabine et al. 2004; Intergovernmental Panel on Climate Change 2007) has also dissolved in the ocean to cause ocean acidification (OA), a much less well-publicized phenomenon. The physical chemistry of OA is very well understood, and these changes have been observed at many locations worldwide. Observational data have contributed to the development and testing of coupled ocean models used to examine climate change and ocean acidification. However, we do not have enough information yet to predict the biological responses to ocean acidification for more than a handful of organisms. As a result, forecasts of the ecological responses to ocean acidification still contain great uncertainty. Predicting OA's socioeconomic effects is also therefore in its infancy. Determining the end-to-end effects of ocean acidification will require a combination of data collection and synthesis, model and method development in multiple disciplines, and intercomparison and linking of earth system, ecological, and socioeconomic models.

CHEMISTRY & OBSERVATIONS

Ocean acidification refers to the suite of chemical changes that occur when excess atmospheric carbon dioxide (CO_2) from human activities reacts with water molecules to form carbonic acid, a weak acid that partially dissociates into hydrogen ions and bicarbonate. Some of the carbon dioxide molecules also react with dissolved carbonate ions that are already present, forming more bicarbonate. The net chemical consequences of these reactions are an increase in hydrogen ions, a decrease in carbonate ions, and an overall increase in the content of dissolved CO_2 species in water. The increase in hydrogen ions increases solution acidity, which also decreases measured pH.

The total quantity of dissolved CO_2 and carbonate system species in seawater, or the inorganic carbon system, can be measured directly or calculated from other observed parameters. Any two of the four parameters including total dissolved inorganic carbon (DIC; the total amount of dissolved CO_2, bicarbonate, and carbonate ions), total alkalinity (TA; the excess base in seawater), pH, and the partial pressure of CO_2 (pCO_2), can be derived from two other measured parameters. Other difficult-to-measure parameters, such as the concentration of carbonate ions and the saturation state of calcium carbonate minerals (Ω), can also be derived similarly. When state-of-the-art methods, standards, and tightly controlled laboratory conditions are used, measured DIC, TA, pH, and pCO_2 have uncertainties ranging from ~0.03%~0.2% (depending on parameter; Dickson, 2009, personal communication). Uncertainties double if analyses are done in less tightly controlled conditions (e.g., at sea). Historically, observational campaigns have usually measured seawater DIC and TA, then calculated pH and pCO_2. Using this method, measurement uncertainties plus error in equilibrium constants yield a combined resultant error of 0.6%-6.3% in derived parameters (Dickson and Riley 1978). The carbonate ion concentration derived by this method has an error of 3.1%; hydrogen ion concentration has an error of 5.6% (Dickson and Riley 1978). Consequently, uncertainty around values of Ω calculated from derived carbonate ion concentrations are of a similar magnitude as the annual rate of change in Ω (-0.09 year^{-1}) observed at time-series stations like ALOHA (Figure 1 in Feely et al. 2009a), which underscores the necessity of long-term ocean acidification monitoring with high-quality measurements.

Seawater chemistry measurements from time-series stations and repeat hydrography cruises show the global extent and progress of ocean acidification. The inorganic carbon chemistry of upper-ocean seawater has been tracked at monthly monitoring locations including ALOHA near Hawaii, BATS near Bermuda, station PAPA in the North Pacific, and ESTOC near the Canary Islands, and records show a progressive decrease in upper-ocean pH, Ω, and/or carbonate ion concentration as seawater CO_2 rises (Dore et al., 2009, updated in Doney 2010; Gruber et al. 2002; González-Dávila et al. 2010). Comparison of datasets from repeat hydrography programs has shown that changes in ocean carbonate chemistry due to the invasion of anthropogenic CO_2 penetrate thousands of meters in each ocean basin (Sabine et al.

2004). Variabilities of pH and pCO_2 are naturally greater in coastal regions because of respiration, photosynthesis, and runoff, so ocean acidification research must also determine what conditions may be damaging there (National Research Council 2010). Numerous programs now focus on establishing baseline conditions in many more locations, such as the Arctic Ocean (Azetsu-Scott et al. 2010; Cai et al. 2010), but infrastructure development is still required to collect enough data to determine baseline conditions and indicate future changes in all regions (Feely et al. 2009b).

Ocean acidification and climate change are also expected to alter other nutrient cycles. Decreases in pH and carbonate ions will affect the solubility, adsorption, toxicity, and rates of redox reactions for metals in seawater (Millero et al. 2009). The biological availability of many metals could change, with varying outcomes: increased copper could kill more phytoplankton, whereas increased iron could support more phytoplankton growth. These changes could be especially important in estuarine biogeochemical cycling, where redox reactions tightly control the behavior of metals and gaseous components like CO_2, which in turn control phytoplankton community composition (Millero et al. 2009). Throughout the oceans, ocean acidification and climate change may also alter nitrogen cycling. Bacterial nitrification could slow as pH decreases and cyanobacterial nitrogen fixation could increase as temperature and CO_2 levels rise, promoting an overall shift towards a larger reduced nitrogen pool dominated by ammonia (Hutchins et al. 2009). At the same time, increasing temperature could slow vertical mixing and thereby reduce upwelling of nutrients from deep water, enhancing nutrient limitation. These consequences of ocean acidification are somewhat less well quantified than the expected changes in pH and carbonate ion concentration, so present OA forecasts primarily focus on inorganic carbon cycle-related changes in the oceans.

EARTH SYSTEM MODELS

Coupled ocean models used to study climate change often include carbon cycles that interact with meteorological variables, oceanographic variables, and biogeochemical processes; therefore, these models simulate ocean acidification as well as other anthropogenically forced changes in Earth systems. Model-data comparisons are used to judge the models' skill at creating hindcasts, and the models that reproduce major features of circulation and tracer transport are believed to provide credible estimates of future climate change at large scales (Intergovernmental Panel on Climate Change 2007). Intercomparison exercises, such as the international Ocean Carbon Model Intercomparison Project (OCMIP), then compare forecasts from multiple skillful models to develop estimates of the range of future conditions. Atmospheric CO_2 levels of ~780 ppm by 2100 (IS92A scenario, Leggett et al. 1992) yielded a median response for OCMIP's thirteen models in which ocean pH decreased by 0.3-0.4 and carbonate ion concentrations dropped globally. Overall, there will be an equatorward contraction and shallowing of high-carbonate waters suitable for animals that make hard shells and skeletons (Orr et al. 2005). Meanwhile, temperature increases due to climate change that decrease CO_2 solubility will counteract less than 10% of the chemical changes associated with ocean acidification (Orr et al. 2005). The subsequent Coupled Climate-Carbon Cycle Intercomparison Project (C4MIP) found that in 11 climate models with land and ocean carbon cycles, feedbacks between climate change and the carbon cycle would occur and increase atmospheric CO2 by an additional ~50-100 ppm, causing additional warming and allied changes (Intergovernmental Panel on Climate Change 2007).

The biogeochemical consequences of future ocean carbon cycle changes are less clear at present. Intercomparison has shown that accurate physics are a very strong determinant of whether modeled biogeochemical processes replicate observed conditions (Doney et al. 2004; Najjar et al. 2007). Detailed intercomparisons of biogeochemical parameterizations in coupled models, though, are often limited for several reasons. First, the level of biogeochemical complexity in the OCMIP/C4MIP models varies greatly, and appropriate evaluation methods and criteria for each model depend on their specific biogeochemical parameterizations. Second, spatially or temporally sufficient data is often lacking for evaluating many modeled biogeochemical processes in detail. Third, modeled biogeochemical parameters (e.g., growth of a generalized pool of zooplankton) are often not directly comparable to observational data (Doney et al. 2009). Most biogeochemical models do undergo qualitative or quantitative model-data

comparison (68%), but there is no standardized approach, and few assessments use in-depth statistical techniques for model-data comparison (Stow et al. 2009). Some models involved in OCMIP and subsequent intercomparison studies have undergone extensive model-data comparison individually. For example, Community Climate System Model (CCSM3) output was evaluated using satellite-derived surface ocean chlorophyll and primary productivity, climatologies of nutrients and pCO_2, and time-series data from observational programs like JGOFS (Doney et al. 2009). This model had the strongest model-data correlations for SST and nutrients, moderate correlations for surface pCO_2 and CO_2 air-sea flux, and weaker correlations for ecosystem variables including chlorophyll, primary production, phytoplankton growth rate, etc. (Doney et al. 2009). Further improvements to the biogeochemical model and its feedbacks may bring the ecosystem variables, which are the most dependent on its parameterizations, into better agreement with observations. To that end, a new model that builds upon CCSM, called the Community Earth System Model (CESM), is being developed and tested (University Corporation for Atmospheric Research 2010). Similar work is underway with other coupled models.

The primary uncertainty in ocean acidification chemistry forecasts comes not from the carbon chemistry itself, measurements, or from coupled models' abilities to predict ocean carbon inventories, but rather from the uncertainty in anthropogenic CO_2 emission trajectories (Intergovernmental Panel on Climate Change 2007). The rate of change of ocean acidification in offshore seawater appears to mirror the rate of atmospheric CO_2 rise (Figure 1 in Feely et al. 2009a). Even if the atmospheric CO_2 trajectory levels off today, ocean pH, surface Ω, and deep-ocean Ω will continue to be depressed compared to preindustrial conditions in the next five centuries (Frölicher and Joos 2010). Long-term forecasts suggest that oceanic uptake of CO_2 will slow as the chemical changes from OA accumulate (Sabine and Tanhua 2010) and as ocean circulation slows from climate change (Intergovernmental Panel on Climate Change 2007), but these factors will not reverse ocean acidification either. Over shorter periods, a moderate amount of uncertainty about ocean acidification's progress in coastal zones is associated with the possibility of changes in freshwater cycling and deposition of other, acid-generating pollutants near shore (Doney et al. 2007; Doney 2010).

BIOLOGICAL RESPONSES & MODELS

Most of the uncertainty about OA's effects on marine ecosystems arises from our present incomplete knowledge about the individual and population-level responses to OA. Any of the chemical changes due to ocean acidification may be biologically relevant (reviewed in National Research Council 2010). The decline in carbonate ions decreases the amount of carbonate building blocks available for marine animals that create calcium carbonate shells and skeletons. These organisms include primary producers such as coccolithophores and coralline algae, zooplankton such as pteropods, mollusks such as clams, oysters, and mussels, crustaceans such as crabs and lobsters, and reef-forming corals. Most of the calcifying organisms studied show negative responses to ocean acidification such as decreasing calcification rates, delayed larval development, and smaller shells (Kroeker et al. 2010). The cellular and organismal mechanisms behind these responses are not yet clear. In other organisms, the decrease in seawater pH, the increase in CO_2, or both may affect concentration gradients of hydrogen ions across cell membranes or change oxygen-CO_2 respiratory balances (National Research Council 2010). Finally, increasing CO_2 concentrations from ocean acidification may benefit photosynthetic organisms like phytoplankton, macroalgae, and seagrasses.

Scaling ocean acidification's effects on individual organisms to populations and ecosystems remains a challenge. Not only will OA's effects on individuals alter their individual performance, but it may also alter their behavior in ways that will generate population-wide consequences. For example, ecosystem-scale observations in natural environments have reported declines in calcifier populations and increases in seagrass populations with increased proximity to CO_2 vents (Hall-Spencer et al. 2008), and shifts from calcifier-dominated communities to photosynthesizer- and invertebrate-dominated communities with long-term pH decreases (Wootton et al. 2008). Until ocean acidification's effects on both life functions and behaviors of susceptible species are known, modeling studies are limited to using

statistical responses generalized from individual studies and falling within trends observed in ecosystem-based studies such as these.

In the absence of mechanistic knowledge of marine organisms' responses to OA, applying statistical relationships describing general responses can still be instructive for providing first estimates of OA's total impacts. Brander et al. (2009) estimated the economic impacts of OA on coral reefs by relating loss of coral cover to ocean acidification using a general relationship summarizing multiple coral studies and an economic value meta-analysis. They concluded that losses were approximately one order of magnitude smaller than those from climate change. However, only broad insight is available from this study because the analysis depends heavily on an assumed linear biological response (loss of coral cover) that may in nature be nonlinear, stepped, or otherwise episodic (Kleypas and Yates 2009). In another analysis, Cooley and Doney (2009) determined the potential losses from ocean acidification to United States commercial mollusk harvests by assuming that calcification rate decreases in mollusks directly correlated to population decreases. They concluded that annual losses in ex-vessel revenue could range from the tens to hundreds of millions of dollars. Their linear damage function approximated trends comparable to those in individual and ecosystem studies, but it did not explicitly include interspecies interactions, adaptability, or long-lasting damage to juveniles, all of which could affect populations over time periods relevant to the analysis. Until more biological data is available, initial studies like these must necessarily use statistical fits instead of mechanistic responses, but these types of studies must be interpreted with care to avoid drawing conclusions broader than the ingoing biological information permits.

CONCLUSIONS & FUTURE WORK

The chemical reactions and equilibria governing carbon dioxide's behavior in seawater have been well understood for decades to centuries, and worldwide observational datasets (e.g., Figure 1 in Feely et al. 2009a) that show decreasing ocean pH and carbonate ion concentration with rising atmospheric CO_2 levels agree with scientific theory. Ocean acidfication's effects on ocean chemistry can be forecast when this well-understood physical chemistry is included in the ocean carbon cycle of coupled ocean models. Intercomparisons of multiple skillful models suggest that ocean acidification will progress globally, and its progression depends greatly on atmospheric CO_2 emissions trajectories. CO_2 emissions, however, depend fundamentally on human behavior, which is far more uncertain. Local factors and climate change will exert secondary control on OA in nearshore regions.

Our ability to forecast ocean acidification's total effects on ecosystems and human economies under different CO_2 emissions scenarios is limited because our knowledge about biological responses to OA is incomplete. We also do not know how ocean acidification will affect coastal ecosystems where marine organisms thrive, although CO_2 concentration and pH variabilities there are already high. We do not know whether ecosystems will undergo stepwise responses or cross tipping points, and we do not understand how best to scale individual effects to population-wide responses.

Until some of these chemical and biological questions are resolved, we will be limited to making broad assessments of potential socioeconomic losses from ocean acidification using observed biological trends. Until then, modeling work must continue to ensure that biogeochemical model skill continues to improve. At the same time, ecosystem models of marine communities like EcoPath and Atlantis must be built, tested, and tuned to permit the extrapolation of biological responses to OA to ecosystems. Finally, socioeconomic studies must find improved ways to value the range of market and nonmarket services that marine ecosystems provide. These parallel efforts will permit skillful biogeochemical models to be linked to ecosystem models and to socioeconomic models.

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