

The role of scientific ocean drilling in understanding ocean acidification

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Introduction

Since the beginning of the industrial revolution, mankind's collective industrial and agricultural practices have caused the release of more than 560 billion tons of carbon as carbon dioxide (CO₂) into the atmosphere. The atmospheric concentration of CO₂ is now higher than experienced on Earth for at least the last 800,000 years and probably over 20 million years, and is expected to continue to rise at an increasing rate. This CO₂ eventually enters the ocean, where chemical reactions will lower the pH and reduce the saturation state with respect to calcium carbonate minerals, such as aragonite and calcite, which are the building blocks for many species of marine plant and animal shells and skeletons. Approximately one third of the CO₂ added to the atmosphere has already been taken up by the ocean. The rate at which the ocean takes up carbon is one of the fundamental factors influencing climate change on the planet. Over thousands of years, most of the carbon dioxide will be neutralized by reaction with these skeletal remains.

The overarching scientific questions that need to be answered in order to understand the fate of CO₂ entering the ocean are – how much can be absorbed, where, how does it spread and how fast is it neutralized? Over a range of time scales from seconds to tens of thousands of years, these chemical changes will influence the climate via the CO₂ that remains in the atmosphere and affect the plants and animals in the ocean.

Time series of environmental and biotic changes preserved in proxy records (e.g., corals and marine sediments) have provided fundamental insights into the carbon cycle,

and have the potential to add new information, leading to a predictive capability that is relevant to policy-makers. First, time series document the amplitude, rate, and timing of natural variability in the system, which span timescales from hours to millions of years. Second, time series from proxy studies provide a measure of the sensitivity of calcification and dissolution rates to the forcing (natural and anthropogenic) from changing saturation states. Finally, time series from geologic proxies provide insights into processes that occur too slowly to be captured by decades-long sets of shipboard and other instrumental measurements. Some of these slow processes appear to maintain steady-state conditions in the ocean, while other processes contribute to the slow evolution of the climate-ocean-environment over millions of years.

In summary, scientific ocean drilling has provided crucial evidence of past changes in the global carbon cycle, that, when integrated with theoretical, process and modeling studies provide scientists with an understanding of fundamental Earth system processes.

Overview of seawater carbonate chemistry

Ocean acidification refers to the lowering of seawater pH from the addition of CO₂. Carbon dioxide entering the oceans dissolves to form carbonic acid, which in turn dissociates to form hydrogen ions, carbonate, and bicarbonate ions. Equilibrium reactions among these and other ions dissolved in seawater maintain the pH of surface seawater at around 8.1. Changes in seawater pH are small because as more carbon dioxide is added, existing carbonate ions are converted to bicarbonate ions. This is termed the buffering effect and has limited the pH change in the oceans caused by the increase in anthropogenic CO₂. Over time, the buffering capacity is reduced as the concentration of carbonate ion decreases, and the pH change becomes larger. Many different plants and animals form skeletons of calcium carbonate. These skeletons are composed of one (or occasionally a combination) of two mineral forms of calcium carbonate (CaCO₃), aragonite and calcite, and they play an important role in the ocean carbon cycle. Corals, most mollusks, some calcareous algae, and some free-swimming animals such as pteropods (planktic gastropods) form aragonite skeletons. Coccolithophores, most foraminiferans, some calcareous algae, echinoderms, and brachiopods form calcitic skeletons. Much of the skeletal material is dissolved soon after being produced, and in particular aragonite is vulnerable to early dissolution. A small fraction remains to accumulate as coral reefs or forms the carbonate fraction of clastic seafloor sediment. The amount of calcite and aragonite preserved depends on the saturation state of seawater, specifically on the carbonate ion concentration relative to the aragonite or calcite saturation state. Furthermore, the rate at which algae and animals calcify (i.e., secrete calcite or aragonite) appears to be dependent on the saturation state of the water in which they live. Understanding and quantifying this sensitivity in different organisms and environmental settings is a principle research objective, as described later. Fundamental controls on the seawater carbonate chemistry are the environmental conditions, including temperature, salinity, and pressure. A more difficult to understand set of controls comes from the

feedbacks and interactions among different processes. None of these processes occur in isolation. For example, the change in the calcification rate influenced by ocean acidification in turn affects the calcium carbonate saturation state of seawater and pH. Another important feedback exists between the amount of dissolved carbonate entering the sea and the amount of carbonate minerals buried on the seafloor. Generally, over thousands of years, a steady state exists between the amount of calcium and carbonate added (principally from rivers) and the amount removed as calcium carbonate sediments, so that the ocean's saturation state remains nearly constant. The timescales for these processes range from seconds for chemical reactions to millions of years for the balance of input and removal, and there is no way to achieve a full understanding without the long records provided by scientific ocean drilling.

Overview of proxies for seawater carbonate chemistry and calcification

Recent development of quantitative proxies for seawater carbonate chemistry and calcification rate augments what can be learned from reconstructing the fraction of calcium carbonate in ocean sediments, rates of accumulation, and other information. With additional development, these proxies could revolutionize our ability to interpret past changes in the ocean carbon cycle. A few promising proxies for seawater carbonate chemistry are listed below. With regard to calcification rate, many of the measurements relied upon in laboratory and field measurements are also useful in scientific ocean drilling studies, including coral extension rate and coral density, plankton shell weight, plankton shell morphology, and variations among different species. Efforts are underway to develop new proxies for carbonate chemistry and calcification. From the perspective of the research questions below, the most important issues are to develop two robust proxies of seawater chemistry allowing all six parameters (pH, total alkalinity, DIC, $p\text{CO}_2$, HCO_3^- , and CO_3^{2-}) to be calculated, and also to improve and calibrate proxies for calcification rates.

Some of the most promising proxies are:

- **pH.** The stable isotope ratio of Boron incorporated into carbonate and aragonite skeletons, including corals, planktic foraminifers, and benthic foraminifers, is sensitive to seawater pH.
- **Dissolved carbon dioxide ($\text{CO}_{2(\text{aq})}$).** The stable carbon isotope ratio of biologically produced particulate organic carbon is influenced by the concentration of dissolved carbon dioxide. This proxy is useful in surface environments, and is further constrained by the measurement of compound-specific fractions of organic carbon such as alkenones.
- **Carbonate ion concentration (CO_3^{2-}).** The incorporation of several different trace metals (including cadmium, zinc, boron, uranium, and magnesium), into skeletal calcite and aragonite has been associated with the carbonate ion concentration and/or saturation state at the seafloor. These trace metal ratios are typically expressed as a concentration relative to calcium (e.g., Cd/Ca).

Past Discoveries

Studies of the carbon cycle and marine biogeochemical cycles are not new to the Integrated Ocean Drilling Program (IODP). One could say these studies have formed a component of most ocean exploration initiatives. Within the “environment theme” of the *IODP Initial Science Plan*, some of the grand questions and some of the successes on these topics are highlighted. Three discoveries are particularly relevant to ocean acidification and are described below.

1. Carbonate accumulation

The relevance of the calcium carbonate accumulating in the sea to biogeochemical cycles, including the carbon cycle, was recognized in the earliest marine geologic expeditions, and has motivated extensive research. The weight percent CaCO_3 remains a basic measure for all samples and has been used to reconstruct the calcite compensation depth (CCD) among many other parameters. One of the difficulties in understanding the weight percent measure is that it reflects a balance between production, dilution (by other sediment components such as clay), and dissolution at the seafloor. Different approaches such as accumulation rate calculations and normalization to constantly accumulating materials can help. Another difficulty lies in understanding the related rain of organic matter, and this is complicated by the observation that generally less than one percent of the organic matter produced is preserved. In this case too, different approaches to reconstruct both carbonate and organic carbon production have found some success. Much of what we have learned about the evolution of ocean environments and ecosystems is derived from the study of carbonate and organic carbon accumulation.

Significance: Calcium carbonate accumulates in sediments as a result of algal and animal production, in diverse ecosystems ranging from coral reefs to the open ocean. Throughout most of the last 100 million years, a balance has existed between the carbonate minerals added by rivers, and the carbonate removed as sediment. This balance contributes to the stability of the Earth climate. Swings in this balance coincide with abrupt climate change (e.g., PETM) as well as slow gradual changes through eons. An abrupt decrease in carbonate saturation is now underway as a result of the addition of anthropogenic carbon, and this is expected to eventually lead to reduced organismal calcification rates and massive dissolution of calcium carbonate in the sea.

2. Glacial cycles of carbon and temperature

The remarkable coincidence of changes in carbon dioxide in the atmosphere and Earth temperature remains one of the great unresolved issues in paleoclimatology, with direct relevance for future climate prediction. Evidence from polar ice cores has

demonstrated that for at least the past 800,000 years, temperatures have risen as the concentration of carbon dioxide has increased, and fallen as the concentration has decreased. For example, during the last Ice Age, 20,000 years ago, carbon dioxide was 30% lower than its pre-industrial concentration, and the mean Earth temperature was 4°C colder. Although the pacemaker for these glacial-interglacial cycles were changes in the Earth's orbit around the sun (the so-called Milankovich forcing) and consequent variations in solar energy distribution across the surface of the Earth, strong positive feedbacks in the Earth system, including in the carbon cycle, must have operated to drive the large temperature swings observed. Based on our current understanding of the sensitivity of climate to atmospheric CO₂ concentrations, about half of the glacial-interglacial climate change can be explained as a direct CO₂ effect. Importantly, proxy data indicate that glacial surface seawater pH was ~0.2 units higher compared to the pre-industrial. Understanding these changes helps calibrate the sensitivity of climate change to carbon dioxide forcing, and may help unravel the feedback processes between carbon and climate that appear to be involved.

Significance: The proxies for seawater chemistry developed so far, and their time series through the Quaternary ice ages, leave no doubt that ocean changes are central to carbon-climate feedbacks that contributed to the ice ages.

3. The PETM

Although the carbonate saturation state of the shallow marine environment has been in approximate steady state over most of the past 100 million years due to buffering processes in the deep sea, there were a few intervals of abrupt change. The largest of these occurred during the Paleocene-Eocene Thermal Maximum (PETM), 55 Ma ago, when an abrupt increase in atmospheric CO₂ caused massive dissolution of shallow carbonate sediments and the extinction of calcifying organisms, primarily pelagic benthic Foraminifera, and possibly corals. The PETM is believed to be a useful analogue for predicting some of the likely future impacts of anthropogenic climate change. In particular, it will provide much needed insight to the rate at which biogeochemical feedbacks will restore the ocean to its pre-anthropogenic state.

Significance: The rapid changes in seawater chemistry that occurred during the brief Paleocene-Eocene Thermal Maximum provide an indication of the massive changes to the ocean environment that will result as anthropogenic carbon dioxide enters the ocean.

Future Research

The goal to understand the fate of carbon entering the ocean has many different components, engaging oceanographers, chemists, modelers, and biologists. The pace of discovery is rapid, and new questions are being formulated. Among many worthy

questions four topics stand out in their urgency and significance to decision-making, and also as being areas where scientific ocean drilling can contribute. These are posed as a research question and a possible approach, and although scientific ocean drilling is mentioned, the emphasis is on an interdisciplinary approach rather than specific drilling targets.

Question 1. What is the natural variability of seawater carbonate saturation state, the long-term trend, and the recent detectable response?

Approach: Reconstruct the past 400 years using corals and high-accumulation rate, marine-sediment cores. The goal is to understand the temporal trends, including the industrial-era changes and the decadal to century scale variability. Premier variables to reconstruct are the saturation state and the rates of calcification, dissolution, and other parameters.

Question 2. What is the sensitivity of biological calcification to the saturation state of seawater?

Approach: Reconstruct calcification rates for different organisms and different time periods that were characterized by different saturation states and different rates of change in saturation. Opportunities exist to exploit the small changes between glacial/interglacial periods, as well as the larger changes found during the PETM and other periods. The most complete approach would compare laboratory, sediment trap, and sedimentary evidence across diverse organisms, including corals, foraminifers, coccolithophores, pteropods, and other marine calcifiers.

Question 3. What are the feedbacks between climate and the ocean carbon cycle?

Approach: One promising approach would focus on the late Pleistocene glacial cycles, for which many proxy estimates already exist. It is clear that the ocean is the only reservoir that could have absorbed carbon to explain the 30% lower glacial atmospheric $p\text{CO}_2$ measured in ice cores. The mechanisms and specific uptake and storage areas, however, are still under debate. Proxy estimates of surface, intermediate and deep-water carbonate chemistry, organic carbon production and deposition, temperature distribution, ocean circulation changes, and many more, are either missing or too sparse to unambiguously identify the controlling factors; however, the community is already making rapid progress in these areas. Comparison with the much larger climate perturbations that occurred during the past 100 Myr can be used to confirm and improve mechanistic models of the ocean-climate feedback system. The transient events such as the PETM provide an opportunity to evaluate the natural rate of sequestration via biogeochemical feedbacks.

Question 4. What are the impacts of sequestration within the ocean or under the seafloor?

Approach: Humans have the potential to engineer the addition of carbon to the ocean using several different sequestration strategies, controlling both the chemical form of the carbon (particulate organic carbon, dissolved carbon dioxide, bicarbonate ions) and the location (shallow, deep, sub-seafloor). Decisions to purposefully sequester carbon require improved understanding of the processes described above (eventually leading to a predictive capability for carbon in the ocean). Sub-seafloor sequestration requires better characterization of the sub-seafloor reservoir. The size and location of potential reservoirs, chemical reactions beneath the seafloor, and fluid flow in permeable rocks are all questions that need to be addressed. Progress in this area would benefit from collaborations between industry and academia.

Critical regions

The cycling of carbon in the ocean varies dramatically among different regions, and a comprehensive approach to the problem will include sampling different environments, different ocean basins, and include transects across environmental gradients. A pragmatic, stepped approach might target four end-member environments for initial study: low-latitude open-ocean environments, high-latitude open ocean environments, shallow water carbonates (including coral reefs), and coastal upwelling areas. An advantage of identifying discrete sites is that other approaches such as moored buoys, ocean observatories, repeat sampling, sediment trap, *in situ* experiments, multi-coring, and ocean drilling can be combined. Sediment proxies are not found everywhere, and the challenge of finding appropriate proxy archives is significant. This problem can be partly remedied through dedicated exploration and additional site surveys (this applies to shallow and deep-water corals as well as marine sediments).

Things to do right now

The infrastructure developed by the Integrated Ocean Drilling Program, ranging from existing core material to international networks of scientific collaborators, provides opportunities for immediate progress on questions 1-4 above, as well as progress on some of the broader aspects of ocean acidification and biogeochemical cycles.

1. Use existing cores

Four decades of scientific ocean drilling have produced an extensive collection of seafloor samples relevant to these questions. For some regions and time periods, for example the PETM described below, insufficient material remains. For other time periods, and for the goal to address broad changes through time, the existing collection could provide a valuable reconnaissance effort.

2. Promote the development and improvement of proxies for seawater chemistry

Improving the proxies for the quantitative reconstruction of seawater carbonate chemistry is needed to fully exploit the record obtained through scientific ocean drilling. Several of the most promising proxies are described in the introduction. All of these need further development to refine the calibrations, understand the limitations and competing influences, and evaluate the uncertainty. Proxies for the saturation state are vitally important because they allow the relationship between calcification rate and saturation to be investigated in the geologic past. Other proxies (for pH, pCO₂) may be added to provide the two parameters needed to reconstruct all aspects of the carbonate system. Two promising proxies for this approach are the B/Ca (a proxy for carbonate ion concentration) and the δ¹¹B (a proxy for pH).

3. Complete the PETM shallow water survey, and replenish depleted sections

Several Ocean Drilling Program legs have focused on recovering the PETM dissolution horizon over the deeper portions of the ocean including Legs 198 and 199 in the North Pacific, and Legs 207 and 208 in the South Atlantic. Additional pelagic depth transects are needed to constrain the carbonate compensation depth (CCD) changes in the Southern Ocean (Atlantic and Indian sectors), as well as in the north Atlantic. The few cores that are available from these regions suggest less extensive carbonate dissolution as observed in lower latitudes. Additional cores are needed to constrain both the depth and spatial dependent changes in the CCD during the PETM. In addition, the full extent of ocean acidification in shallow marine environments is unknown due to the lack of cores from the continental margins. As a consequence, future drilling must focus on recovery of the PETM from hemi-pelagic to coastal depositional facies.

4. Exploit recent and planned IODP expeditions to drill submerged coral reefs

There are three recent, planned, or proposed IODP expeditions that target submerged coral reefs. These are Expedition 310, which drilled in Tahiti in 2005, Expedition 325, which is scheduled to drill on Australia's Great Barrier Reef in late 2009, and a proposal for a drilling expedition to drill in Hawaii (currently under consideration). In each case the focus is to sample glacial and de-glacial coral reef sequences. Major objectives of these studies are to improve our understanding of sea level changes as the

Earth's climate moves from glacial to interglacial conditions, and to elucidate the role of the tropical oceans in driving or regulating global climate variability and change. However, the samples collected have significant potential to help address outstanding questions relating to the impact of changes in atmospheric CO₂ on aragonite saturation state and on coral reef communities. First, geochemical analysis of the skeletons of reef-building organisms may provide new estimates of changes in sea water pH (and its variability) during the last (and potentially earlier) glacial interval and through the deglaciation. The success of this approach will depend on development of relatively new proxies including $\delta^{11}\text{B}$ in coral aragonite. Second, through retrospective analysis of the calcification rate of annually banded corals sampled in the cores (measured as linear extension rate times the bulk density), it may be possible to assess the relative impact of the inferred past changes in aragonite saturation state on coral growth. This is likely to be a challenging task, requiring analysis of large numbers of coral fragments and careful consideration of the separate influences of changes in other variables such as temperature, but could provide important new constraints on the impacts of changing atmospheric CO₂ over timescales of hundreds to thousands of years. Finally, changes in reef community composition through time recorded in the skeletal remains in the cores may be interpreted in the context of changes in the physical and chemical environments on the reefs, including changes in carbonate saturation state and other aspects of the marine carbon cycle.

5. Advance an integrated sampling strategy that includes other efforts in addition to drilling

Valuable samples can be obtained, and rapid progress achieved, by utilizing sampling approaches in addition to drilling. For the deep sea, multi-coring and giant piston coring are useful complementary approaches. For coral reef environments, diving and sampling via remotely operated vehicles add to the types of samples that can be collected. These approaches provide access to high-resolution archives capable of reconstructing changes in ocean carbonate chemistry, skeletal calcification rates, and ecosystem changes over the past decades to millennia. Through this route, IODP has the potential to deliver the rate of progress that is required in these areas to help inform crucial near-term policy making decisions.

Partnerships

Scientific ocean drilling can contribute to ocean acidification initiatives now underway, and would benefit from partnering with these efforts. On an international scale, the Ocean Acidification Network, the European Project on Ocean Acidification (EPOCA), and the International Ocean Carbon Coordination Project (IOCCP), and the Integrated Marine Biogeochemistry and Ecosystem Research (IMBER) all exist to coordinate ocean acidification and related research. Within the U.S., the U.S. Ocean Carbon and Biogeochemistry Program (OCB) has an ocean acidification subcommittee,

and several agencies (including NOAA and the USGS) have expanding programs on this topic.

The two most important near-term partnering opportunities are to integrate the emerging best practices being developed by the groups described above into proxy development and paleo-calibration studies, so that paleo-reconstructions are of highest quality and can be integrated with modern observations. Of particular interest is the *Guide to Best Practices in Ocean Acidification Research and Data Reporting* now being prepared. Secondly, scientists should seek to identify research questions within each of these initiatives where drilling can play a unique role. In the longer term, as the Ocean Observatories Initiative (OOI) gets underway, additional opportunities may arise to create an observing network that links long geologic time series with real-time observing networks.

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