

## OCB-OA: Forecasts

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### Why wasn't this 'Ocean Acidification' problem predicted earlier?

*Basic:* The ocean acidification problem was first predicted in the early 1970s when it was recognized that continued burning of fossil fuels would cause higher concentrations of CO<sub>2</sub> in the mixed layer of the ocean and decrease carbonate mineral saturation states (Zimen & Altenhein, 1973; Fairhall, 1973; Fairhall & Erickson, 1975). Scientists recognized the potential biological consequences for CaCO<sub>3</sub>-forming organisms, and that the consequences of ocean acidification would drastically effect organisms that build their skeletons and shells from calcium carbonate minerals and create disturbances in ecological systems in the sea (Zimen & Altenhein, 1973; Fairhall, 1973; Fairhall & Erickson, 1975). However, these concerns were not really followed up on until the 1980's when field observations were first used to calculate the effect of uptake of excess CO<sub>2</sub> in the northeast Pacific Ocean on carbonate chemistry (Betzer et al. 1984, Byrne et al. 1984, Feely and Chen 1982, Feely et al. 1984, Feely et al. 1988). In the 1990s coral reef biologists started to test the hypothesis that changes in seawater chemistry from ocean acidification affects the ability of marine organisms to produce their shells and skeletons out of calcium carbonate minerals—see Kleypas et al. (1999) and Langdon et al. (2000) and papers cited therein, as well as Riebesell et al. (2000). The complexities of understanding OA are indicative of the significant disciplinary boundaries that existed between marine chemistry and marine biology and which even now are only slowly being broken down as we develop multidisciplinary research projects to assess the likely consequences of ocean acidification.

*Intermediate:* The ocean acidification problem was first predicted explicitly in the early 1970s when it was recognized that continued burning of fossil fuels would cause higher concentrations of CO<sub>2</sub> in the mixed layer of the ocean and decrease carbonate mineral saturation states (Zimen & Altenhein, 1973; Fairhall, 1973; Fairhall & Erickson, 1975). In the paper of Fairhall (1973) and in a paper written criticizing it (Whitfield, 1974) the key concern articulated by these geochemists was to ask if and when the surface oceans might become undersaturated with respect to CaCO<sub>3</sub>. There was discussion as to the likely ocean pCO<sub>2</sub> in the 21<sup>st</sup> century and some skepticism as to the likely consequences. Scientists emphasized the potential biological consequences for CaCO<sub>3</sub>-forming organisms, recognizing that the consequences of ocean acidification would drastically effect organisms that build their skeletons and shells from calcium carbonate minerals and create disturbances in ecological systems in the sea (Zimen & Altenhein, 1973; Fairhall, 1973; Fairhall & Erickson, 1975). It is interesting to note that these concerns were not really followed up on until the 1980's when field observations were first used to calculate the effect of uptake of excess CO<sub>2</sub> in the northeast Pacific Ocean on carbonate chemistry, and calcite and aragonite saturation horizons (Betzer et al. 1984, Byrne et al. 1984, Feely and Chen 1982, Feely et al. 1984, Feely et al. 1988). In the 1990s coral reef biologists started to test the hypothesis that saturation state controls calcification in corals and marine calcareous algae (rather than it depending simply on whether the waters were under- or oversaturated with respect to CaCO<sub>3</sub>)—see Kleypas et al. (1999) and Langdon et al. (2000) and papers cited therein, as well as Riebesell et al. (2000).

Those earlier studies led scientists to test a wider variety of organisms where it was felt that ocean acidification-induced changes in seawater chemistry might play a role. As more and more organisms are studied, it is apparent that many do not take well to life in higher CO<sub>2</sub> waters. Nevertheless, even now there are cautions. First, in early experiments there was often a mismatch between the exposure conditions in laboratory experiments and those (typically more variable) conditions that are expected to occur in nature. More recent experiments more closely mimic the changes expected to occur in the future. However, only few species and ecosystems have been examined. Second, scientists are uncertain as to which species, if any, will be able to adapt to changing atmospheric and ocean chemistry conditions. Finally, it is also uncertain as to how the species composition of whole ecosystems will change as individual organisms find life more stressful than they had in the past. There is still much that we don't know about the effects of ocean acidification, and it remains unclear as to how to manage for resulting changes in the future.

It is really unknown as to why these early warnings from the 1970s—in many ways prescient, in others simplistic—were essentially ignored even by marine chemists and modelers (e.g., Caldeira & Wickett, 2003). It is perhaps indicative of the significant disciplinary boundaries that existed between marine chemistry and marine biology and which even now are only slowly being broken down as we develop multidisciplinary research projects to assess the likely consequences of ocean acidification. The complexities of understanding OA are indicative of the significant disciplinary boundaries that existed between marine chemistry and marine biology and which even now are only slowly being broken down as we develop multidisciplinary research projects to assess the likely consequences of ocean acidification.—A. Dickson, K. Yates

*Advanced:* The ocean acidification problem was first predicted explicitly in the early 1970s. Two authors in particular emphasized the potential biological consequences for CaCO<sub>3</sub>-forming organisms:

“. . . the increase will ultimately reach 200 to 300% if mankind burns all the fossil fuels during the next century. Long before this, there

would certainly be intolerable disturbances of the ecological systems in the sea. If the predicted consequences are substantiated by marine chemists and marine biologists, the  $\text{CO}_2$  problem—and hence the energy problem, too,—will have to be seen in a new dimension.” (Zimen & Altenhein, 1973)

“Thus the concentration of in the mixed layer will diminish with time as fossil fuel is absorbed, until the mixed layer will become undersaturated with respect to aragonite and calcite. The sea is presently supersaturated with respect to these minerals which calcareous organisms form in building their shells. Should the sea become undersaturated in  $\text{CaCO}_3$  the shells of these organisms would tend to dissolve, as would the ocean’s coral reefs. The consequences could be very serious for life in the sea.” (Fairhall, 1973)

“It would also be of interest to know the response of the calcareous organisms to high ambient partial pressures of  $\text{CO}_2$  sufficient to produce undersaturation with respect to  $\text{CaCO}_3$ . Two questions require answers: can these organisms build their shells at all under undersaturated conditions; if so, what is the kinetics of the heterogeneous redissolution reaction—can the shells remain undissolved during the lifetime of the organisms. It would be reassuring if the answers to these questions were affirmative.” (Fairhall, 1973)

“At mid to high latitudes the average sea temperatures are much lower and these areas would be the first to achieve undersaturation of aragonite with increase of  $P_{\text{CO}_2}$ . Fortunately the majority of calcareous organisms that flourish in the cold, subtropical seas are calcitic, and therefore less soluble; but aragonitic forms do occur.” (Fairhall & Erickson, 1975)

As can be seen, particularly in the paper of Fairhall (1973) and in a paper written criticizing it (Whitfield, 1974) the key concern articulated by these geochemists was to ask if and when the surface oceans might become undersaturated with respect to  $\text{CaCO}_3$ . There was discussion as to the likely ocean  $p(\text{CO}_2)$  in the 21<sup>st</sup> century and some skepticism as to the likely consequences:

“The biological implications of such a change are unknown. The attainment of the saturation level may in itself be less significant than the accompanying fall in the pH of the mixed layer. (Whitfield, 1975).”

It is interesting to note that these concerns were not really followed up on until the 1980’s when field observations were first used to calculate the effect of uptake of excess  $\text{CO}_2$  in the northeast Pacific Ocean on carbonate chemistry, and calcite and aragonite saturation horizons (Betzer et al. 1984, Byrne et al. 1984, Feely and Chen 1982, Feely et al. 1984, Feely et al. 1988). In the 1990s coral reef biologists started to test the hypothesis that saturation state controls calcification in corals and marine calcareous algae (rather than it depending simply on whether the waters were under- or oversaturated with respect to  $\text{CaCO}_3$ )—see Kleypas et al. (1999) and Langdon et al. (2000) and papers cited therein, as well as Riebesell et al. (2000).

Those earlier studies led scientists to test a wider variety of organisms where it was felt that ocean acidification-induced changes in seawater chemistry might play a role. As more and more organisms are studied, it is apparent that many do not take well to life in higher  $\text{CO}_2$  waters. Nevertheless, even now there are cautions. First, in early experiments there was often a mismatch between the exposure conditions in laboratory experiments and those (typically more variable) conditions that are expected to occur in nature. More recent experiments more closely mimic the changes expected to occur in the future. However, only few species and ecosystems have been examined. Second, scientists are uncertain as to which species, if any, will be able to adapt to changing atmospheric and ocean chemistry conditions. Finally, it is also uncertain as to how the species composition of whole ecosystems will change as individual organisms find life more stressful than they had in the past. There is still much that we don’t know about the effects of ocean acidification, and it remains unclear as to manage for resulting changes in the future. The complexities of understanding OA are indicative of the significant disciplinary boundaries that existed between marine chemistry and marine biology and which even now are only slowly being broken down as we develop multidisciplinary research projects to assess the likely consequences of ocean acidification. —A. Dickson, K. Yates

### Would seawater ever become acidic, even if all the world's fossil fuel reserves were burned?

*Basic:* Probably not. Using all of the known reserves of fossil fuels would not release enough  $\text{CO}_2$  to make the surface oceans acidic ( $\text{pH}<7$ ). The chemistry of the ocean carbon system also works to prevent a widespread, dramatic pH drop like this. But burning all fossil fuel reserves could release methane hydrates through warming, which could then be used by microbes to generate  $\text{CO}_2$  and possibly make some areas of the ocean become acidic.

*Intermediate:* Probably not. If all of the known recoverable reserves of coal, oil and natural gas are burned over the next two centuries it still does not release enough carbon dioxide to make the surface oceans become acidic. Moreover, the fundamental chemistry of the ocean carbon system, including the presence of calcium carbonate minerals on the ocean shelf and slope floor that can slowly dissolve and help neutralize some of the  $\text{CO}_2$ , prevents the oceans from becoming acidic on a global scale. However, if we also consider the vast stores of methane hydrates in ocean sediments, which can become unstable as ocean temperatures warm, the picture may change. If there were to be a massive release of methane from these sedimentary hydrates, the oxidation and subsequent production of  $\text{CO}_2$  could

be enough for some regions of the ocean to actually become acidic (Caldeira and Wickett 2005). —C.L. Sabine, J. Mathis, R. Feely

### Which affects ocean acidification more, the rate or the amount of carbon dioxide released?

*Basic:* Over the next 50 years, different rates of CO<sub>2</sub> release don't affect the consequences for the earth system very much. But after that, rates of emissions do affect the level of ocean acidification. In the end, the total amount of CO<sub>2</sub> released will affect how low ocean pH goes and how long it lasts.

*Intermediate:* This is a complex question because both are important in determining the extent of ocean acidification over the next few centuries. Model projections show very little difference in the rate of CO<sub>2</sub> emission under differing scenarios for the next 50 years.

However, after that there is a considerable divergence in the model outputs that show an order of magnitude difference in the amount of CO<sub>2</sub> released based on different emission scenarios. This is when we would expect to see the greatest differences in the overall ocean acidification effects. In the near term, the rate of emission will likely have the greatest impacts on those organisms that are forced to adapt to a quickening change in their environment. In the long run though, the total volume of CO<sub>2</sub> emitted is what will ultimately determine how low ocean pH drops and how long these changes will persist in the environment. —J. Mathis, R. Feely

### How strong is OA in my region and how might it develop in the future?

*Basic:* We are still gathering data to measure how strong OA is everywhere. But certain things make some regions more likely to experience ocean acidification. For example, some upwelling sites also have local circulation that makes ocean acidification more intense there. High-latitude oceans already have low saturation states, so further decreases might push them past a harmful threshold.

*Intermediate:* While ocean acidification is a global problem that will affect every single region at some point, there are places that are more sensitive and susceptible to its effects in the near term. For example, regions where there is natural upwelling of deep water onto the continental shelves, such as the west coast of North America, will be particularly vulnerable to ocean acidification. Other hot spots exist in the high latitude oceans near both poles. These regions are colder, which means higher concentrations of CO<sub>2</sub> and in most cases they are naturally preconditioned to have lower pH due to ocean mixing patterns or unique physical and chemical processes. If you live in a region where one or more of these processes exacerbate the ocean acidification effect then the impacts will likely be sooner rather than later. —J. Mathis, R. Feely

### How long it will take the ocean to recover from recent ocean acidification?

*Basic:* After seawater absorbs CO<sub>2</sub> from the atmosphere, its pH and other chemistry have changed measurably. The seawater needs to react with calcium carbonate minerals to overcome this ocean acidification. Calcium carbonate minerals are common on the sea floor and in rocks on land. But it takes about one thousand years for all the seawater in the ocean to circulate from the surface to the deep ocean and around the world.

*Intermediate:* The increased levels of seawater CO<sub>2</sub> from human emissions (anthropogenic CO<sub>2</sub>), which causes ocean acidification, builds up in the upper portions of the ocean and is slowly transported to deeper depths via mixing and convective processes as part of the global circulation "conveyor belt." These CO<sub>2</sub>-enriched waters must eventually react with calcium carbonate minerals in sediments in order for the excess CO<sub>2</sub> to be neutralized and carbonate alkalinity restored back into the water column. Ocean surface waters are not in contact with enough carbonate minerals in shallow sediments to allow total equilibration; thus equilibration of the ocean with carbonate minerals in deep-sea sediments necessarily involves deep-ocean circulation processes that take thousands of years to occur. Reaction of anthropogenic CO<sub>2</sub> with carbonate minerals will ultimately cause the average ocean alkalinity to get back into balance; however, full recovery of the oceans will require tens to hundreds of thousands of years. —R. Feely

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