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OCB-OA: Geological processes and history

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How do we know what ocean pH was in the past?

Basic: We use “proxies” to look at the historical pH record. These are characteristics preserved in ice sheets or layers of sediment on the ocean floor that can be directly measured. Proxies can be related mathematically to characteristics that weren’t preserved, like pH. Proxy records of air bubbles trapped deep in ice sheets and skeletons of marine plankton show that the surface ocean pH stayed around 8.1 for millions of years.

Intermediate: Studying past marine environmental conditions is the focus of paleoceanography, a field that uses stand-ins or “proxies” for parameters that can no longer be measured, but that hold a close relationship to another measurable quantity. For the last 800,000 years, scientists have calculated ocean pH using the CO_2 concentration of air bubbles trapped in glaciers during ice sheet formation. In pre-industrial times the CO_2 concentration of the atmosphere followed the CO_2 concentration of the world surface ocean because of Henry’s law. We can then calculate the ocean CO_2 content from these air bubbles using the same relationship and then estimate ocean pH from that number. In fact, the ice core record shows that the atmospheric CO_2 concentration has never been higher than about 280 ppm during the last 800,000 years, creating conditions leading to an average preindustrial surface ocean pH of ca. 8.2.

To determine what ocean pH was more than 800,000 years ago, paleoceanographers use other proxies, such as the chemical and isotopic composition of fossil carbonate shells. In particular, the uptake of boron and its isotopes into foraminifer (microplankton that produce calcite shells) shells and coral skeletons are indicators for past seawater pH: Because the relative abundance of two dissolved species of boron in seawater, boric acid and borate, depend on seawater pH and because the relative abundance of boric acid increases at lower pH, marine carbonates incorporate relatively less boron and with a lower isotopic composition under low-pH conditions. Other proxies for marine carbonate chemistry include U/Ca ratios, and in shells of benthic foraminifers, also Zn/Ca and Cd/Ca ratios. All these chemical and isotopic proxies provide independent evidence for changes in seawater acidity in the growth environment of marine calcifiers. Using just the presence or absence of calcifying marine organisms in the geological record is not a good indicator for ocean acidification because the absence of carbonaceous remnants at the seafloor does not necessarily mean that the organisms did not live in the surface (calcifying planktonic organisms) or even the deep ocean (calcifying benthic organisms). Calcium carbonate structures could just have been dissolved at the sea floor as a consequence of the mineral’s solubility, which is determined by the seawater’s temperature, pressure, and amount of dissolved CO_2. — J. Bijma, B. Hönisch, J. Mathis, R. Feely

If rock weathering increases, will this offset OA somewhat?

Basic: Increasing weathering of continental rock and transport of its dissolved constituents to the ocean counteract acidification of seawater, but weathering rates are so slow that this process is only important on timescales of tens to hundreds of thousands of years.

Intermediate: Over thousands of years, the weathering of continental rocks does increase the alkalinity of seawater and increases its ability to counteract pH decreases, but neutralizing all of the CO_2 from human activity that is entering the oceans with this process alone would take tens of thousands of years. Therefore, on the time scales of importance to humankind (decades to centuries), these processes are not fast enough to significantly buffer ocean acidification.—F. Mackenzie, B. Hönisch, R. Zeebe, R. Feely, J. Bijma

Advanced: Future increase in atmospheric CO_2 and temperature could enhance weathering of continental calcium carbonate ($CaCO_3$) and silicate ($CaSiO_3$) rocks (Walker et al., 1981; Berner et al., 1983):

$$CaCO_3 + CO_2 + H_2O = Ca^{2+} + 2HCO_3^-$$

$$CaSiO_3 + 2CO_2 + H_2O = Ca^{2+} + SiO_2 + 2HCO_3^-$$

Increased flux of conservative cations from this process to the ocean will increase ocean total alkalinity, and thus, buffer seawater pH. Total alkalinity is essentially a measure of the acid neutralization capacity of seawater. However, the rate of weathering would have to increase *dramatically* to offset ocean acidification on the time scale of the problem, which is not likely under the projected scenarios of rising atmospheric CO_2 and temperatures. The present day flux of total alkalinity to the ocean from weathering on land is about 0.4×10^{15} g yr^{-1} (Mackenzie and Lerman, 2006). Even a very unlikely doubling of this flux would take hundreds of thousands of years to neutralize

all the CO_2 entering the ocean from human activities. Uchikawa and Zeebe (2008) have predicted that the average surface ocean pH will decrease by 0.64 to 0.78 units owing to emissions of 5,000 Pg C under a scenario of a weak weathering feedback. Under a scenario of strong weathering, the corresponding decline is 0.60 to 0.77 pH units. Thus, on the time scale of significance of human generations (decades to centuries), potential increases in continental weathering rates are not fast enough to buffer OA significantly. (See also *OA Primer* section) —F. Mackenzie, B. Hönisch, R. Zeebe, R. Feely, J. Bijma

As ocean acidity rises, will minerals underwater dissolve and offset ocean acidification?

Basic/Intermediate: Some minerals, in particular calcium carbonate ($CaCO_3$) minerals, will tend to dissolve under progressively more acidified conditions. In general, this source of neutralization will be too slow to offset ocean acidification, except to drive a global recovery of ocean pH over thousands of years.—A. Andersson, D. Archer, R. Feely, B. Hönisch

Advanced: Observational and experimental evidence suggest that dissolution of calcium carbonate minerals will increase in both the deep and shallow ocean in response to ocean acidification (Feely et al., 2004; Andersson et al., 2009; Tribollet et al., 2009; Olafsson et al., 2009). Because the process of $CaCO_3$ dissolution generates total alkalinity ($CaCO_3 + CO_2 + H_2O = Ca^{2+} + 2HCO_3^-$), this process has potential to counteract anthropogenic ocean acidification and buffer seawater pH. Nevertheless, in order to significantly buffer the seawater pH for any given system, the rate of $CaCO_3$ dissolution needs to be sufficiently fast relative to the ocean uptake of anthropogenic CO_2 and physical mixing processes to allow for total alkalinity to accumulate and increase in the ocean as a whole (Andersson et al., 2005; Morse et al., 2006; Andersson and Mackenzie, 2012). On timescales of decades to centuries, $CaCO_3$ dissolution will be too slow to produce sufficient total alkalinity to significantly offset ocean acidification (Andersson et al., 2003; Morse et al., 2006). Nonetheless, on timescales of several thousands of years, dissolution of carbonate sediments in both shallow coastal waters and, most importantly, the deep ocean will act as the ultimate sink of anthropogenic CO_2, by providing the antacid or buffer for the world ocean (Archer et al., 1998; Broecker, 2003; Archer et al., 2005).—A. Andersson, D. Archer, R. Feely, B. Hönisch

Why would OA cause extinctions if species have survived changes throughout geological history?

Basic: Other than at times of great mass extinctions, there is no evidence in the geologic record for sustained rates of change in atmospheric CO_2 that have been as great or greater than today's. During mass extinction events that have occurred in Earth's history when climate change caused changes in ocean chemistry, the number of marine species was severely reduced. The number of species that survived represents only a small number of those that were present before the change. It takes millions of years for new species to arise, and adaption of those that survived to increase the number of species back to the same level as before the extinction event.

Intermediate: The danger from ocean acidification is related to the current rate of change, the concentration of atmospheric CO_2 expected, and the magnitude of change of atmospheric CO_2 forecast if we keep emitting CO_2 at the same rate. Additionally, one must consider how rapid environmental change can affect organisms and species diversity. Today's rate of CO_2 increase in the atmosphere is approximately 100 times greater than most changes that have occurred previously in Earth's history. Other than at times of the great mass extinctions, there is no evidence in the geologic record for sustained rates of change in atmospheric CO_2 that have been as great or greater than today's. During mass extinction events that have occurred periodically in geologic history due to climate change, the diversity of marine species was severely reduced. The number of surviving species represents only a fraction of the diversity of organisms that was present before the change. Recovery of species from these events is due to adaptation of the few existing species and evolution of new species. However, it takes several million years to achieve pre-extinction levels of biodiversity.—J. Barry, D. Schmidt, K. Caldeira, P. Hallock Muller

Full Technical: The danger from ocean acidification is related to the current rate of change, the concentration of atmospheric CO_2 expected, and the magnitude of change of atmospheric CO_2 forecast if we keep emitting CO_2 at the same rate. Additionally, one must consider how rapid environmental change can affect organisms and species diversity. The present rise in atmospheric CO_2 is ~2 ppm per year, and atmospheric CO_2 has increased more than 100 ppm since the beginning of the Industrial Revolution. In the transition between the end of the last ice age to the current warm period, CO_2 concentrations increased 80 ppm over more than 10,000 years (Shakun et al. 2012). Today's rate of CO_2 increase in the atmosphere is, therefore, approximately 100 times greater than most changes sustained over geologic time. Other than at times of the great mass extinctions, there is no evidence in the geologic record for sustained rates of change in atmospheric CO_2 that have been as great or greater than today's. Even during extreme ocean chemistry changes in geological history—- for example, during the Paleocene/Eocene thermal maximum 55 million years ago (Ma) when carbonate minerals dissolved in most of the deep and intermediate ocean—-these changes happened over several thousands of years (Zachos et al. 2005). Estimates for the Permian-Triassic mass extinction event exceed 90% of marine species (Benton and Twitchett 2003). Estimates for extinction of species at the end –Cretaceous event vary with different kinds of organisms (MacLeod et al. 1997). Of the planktonic foraminifers and coccolithophores, which are marine protists that produce shells or plates from calcium carbonate minerals, roughly 80% of species

became extinct. For corals, the estimate is about 60% of species and more than 90% of colonial corals that build reefs. So “many” survivors of past changes in ocean chemistry in reality represented only a fraction of the diversity of organisms present before the change. In general, ocean life recovers from extinction episodes by adaptation and evolution of new species, but this takes approximately 10 million years to achieve pre-extinction levels of biodiversity. —J. Barry, D. Schmidt, K. Caldeira, P. Hallock Muller

How is today's change in ocean chemistry different from those in the past?

Basic: Estimated past rates of atmospheric CO_2 changes were considerably lower than today (by about 100 times). This means there was enough time for the ocean to remove the CO_2 from the surface ocean to the sea floor in calcium carbonate sediments. Because the CO_2 levels were changing much more slowly than the ocean was mixing, the systems could keep them in balance. The opposite is true today, with CO_2 being added to surface waters more quickly than it can be mixed through the ocean and reacted with calcium carbonate sediments, making the ocean more acidic and at a faster rate.

Intermediate: CO_2 is currently being added to the surface ocean much more quickly than geological processes can remove it. On timescales of about a thousand years, ocean currents mix and dilute the CO_2 added to the surface of the ocean with the much larger volume of water in the deep ocean. On timescales of several thousand years, CO_2 is removed by reaction with sediments made of calcium carbonate. In the past, CO_2 was typically added to the ocean surface (for instance by volcanoes) at about the same rate that the processes above removed it. Today the rate of CO_2 addition by humans is about 100 times faster, so CO_2 is being concentrated in surface waters, causing a larger and more rapid change in ocean pH. —J. Rae, C. Langdon, A. Ridgwell, R. Zeebe, D. Schmidt

Advanced: The current rate of CO_2 addition to the surface ocean is likely unprecedented in the geological record (Caldeira & Wickett, 2003; Hönisch et al., 2012). This is driving a particularly dramatic change in ocean carbonate chemistry, because the rate of CO_2 addition is significantly higher than the rates of the mitigating geological processes.

The first of these processes is deep ocean circulation and mixing (Broecker & Peng, 1982). On timescales of several hundred to thousands of years, ocean circulation mixes the CO_2 that is added to the relatively small volume of water in the warm surface ocean (above the thermocline) with the much larger volume of water in the cold deep ocean. Most CO_2 additions in the geological past were slow enough that this process mixed (and thus diluted) CO_2 throughout the whole ocean, so the resulting pH change was minor. Today’s CO_2 release is sufficiently fast that 50% of anthropogenic CO_2 is concentrated the top 400 m of the ocean (Sabine et al. 2004), causing a much larger pH change within the habitat of most marine organisms.

The second mitigating process is dissolution of calcium carbonate in deep ocean sediments (see Archer et al. 2009). This takes place on timescales of ~10,000 years, and has the effect of removing CO_2, via the (simplified) reaction: $CO_2 + CaCO_3 + H_2O \Rightarrow Ca^{2+} + 2HCO_3^-$. On geological timescales this reaction acts to increase ocean pH and $[CO_3^{2-}]$ back towards the levels they were prior to an initial CO_2 addition, and also causes an extra increase in $CaCO_3$ saturation state (?; a key parameter in biomineralization), due to the addition of Ca^{2+} (as ? = $[Ca^{2+}].[CO_3^{2-}]/k_{sp}$); see Honisch et al. (2012). In contrast, today’s CO_2 addition is happening too quickly for this buffering reaction to occur, so pH and ? in surface ocean waters are falling more rapidly, and by a larger amount, than in the geological past. This may be problematic for organisms that have evolved in an ocean that experienced smaller and slower changes in ocean chemistry (Ridgwell & Schmidt 2010). —J. Rae, C. Langdon, A. Ridgwell, R. Zeebe, D. Schmidt

How will OA affect the particles reaching the seafloor and the geological record?

Basic/Intermediate: If OA persists long enough, the overall accumulation of $CaCO_3$ on the sea floor will be reduced because of decreasing rates of calcification by marine calcifiers living in the water column and on the bottom, but also due to increasing dissolution of $CaCO_3$ in the sediments. At locations on the seafloor where $CaCO_3$ dissolves faster than new $CaCO_3$ is added, a sediment core in the future will likely display a dark brown layer for this time period (Figure 5).

Advanced: It is very likely that if OA persists long enough that the overall accumulation flux of $CaCO_3$ on the sea floor will be reduced because of (1) decreased benthic calcification rates and enhanced dissolution rates, particularly of skeletal aragonite and magnesian calcites, in shoal-water carbonate ecosystems, e.g., reefs, and (2) decreased pelagic coccolithophore (calcite) and pteropod (aragonite) calcification rates and enhanced dissolution, particularly of pteropods, as the carbonate saturation horizons rise toward the surface of the ocean. In turn, because of the decreased $CaCO_3$ flux, the flux of organic matter to the seafloor will decelerate because of the weakening of the ballasting effect of the $CaCO_3$, (Klaas and Archer, 2002) potentially slowing the rate of removal of CO_2 from the atmosphere (Gehlen et al., 2011).

How a sediment core will look depends on where the core was taken. For example in a polar to subpolar region where current pteropod population densities are high, the core might exhibit evidence of a cessation of $CaCO_3$ deposition, a hiatus. This will likely encompass itself as a dark brown layer in which all the white $CaCO_3$ have dissolved away (Figure X). Such a layer is found from the time of the Paleocene Eocene thermal maximum (PETM), 55 million years ago, caused by a release of carbon analogous to fossil fuel CO_2 (Zachos et al., 2005; Kump et al., 2009). For the oceans as a whole on the present time scale, sediment cores might become more calcite rich as accumulation rates of the more soluble aragonitic and magnesian calcitic fractions decrease. A global mineralogy more similar to the "calcite seas" of the past might develop. —F. Mackenzie, D. Archer

Figure 5: Ocean acidification in sediment cores. The marine geological signature of an ocean acidification event as it might get recorded in a sediment core. The figure shows both results from a model simulation and data from the Paleocene-Eocene Thermal Maximum. From Kump et al., 2009, *Oceanography*.

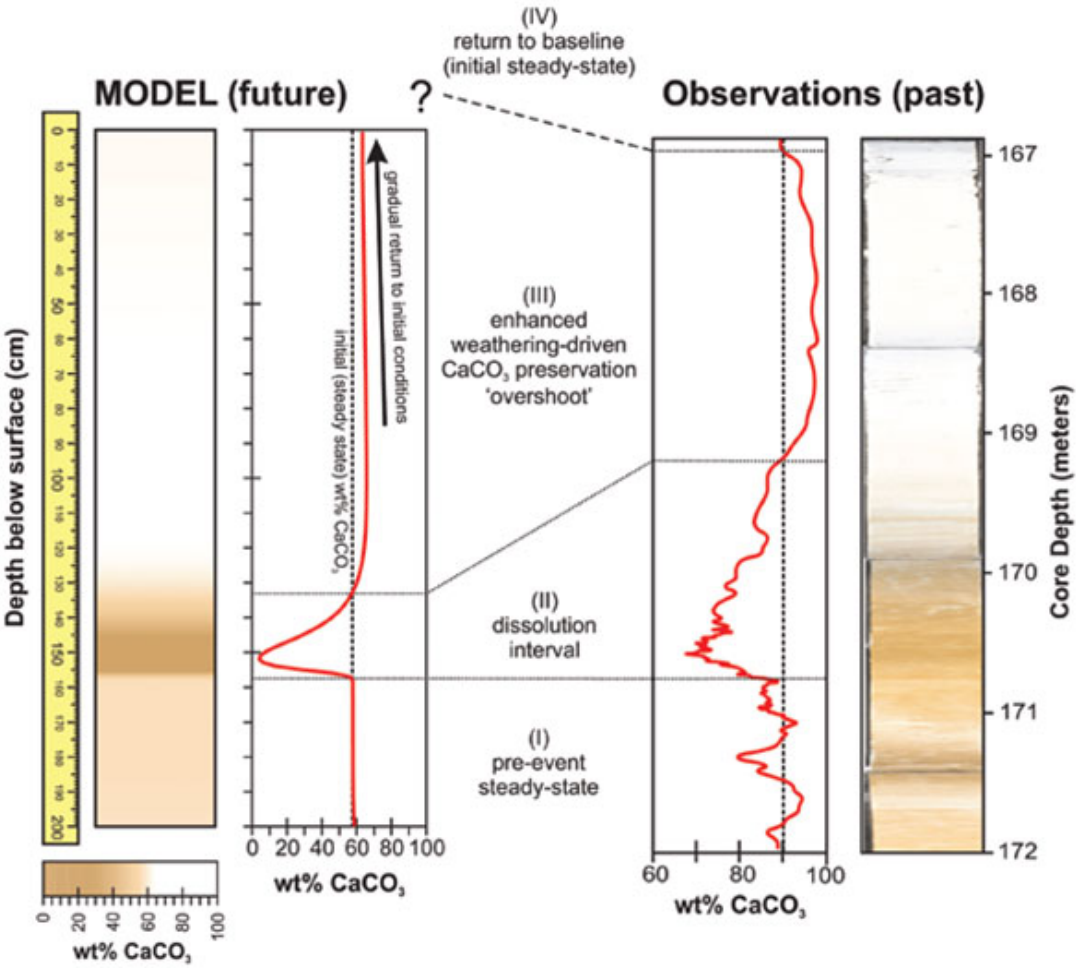
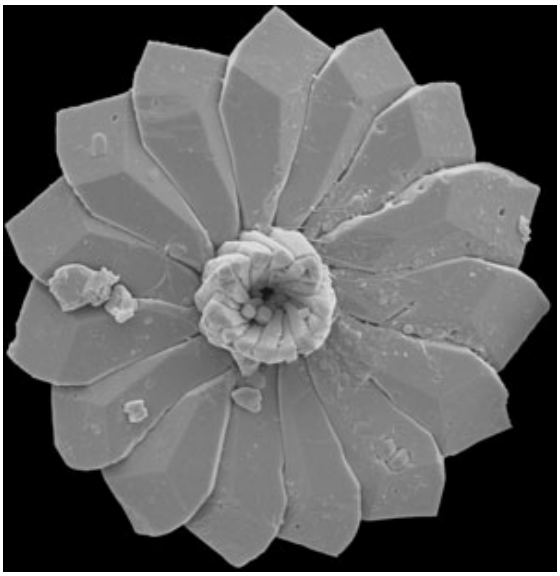
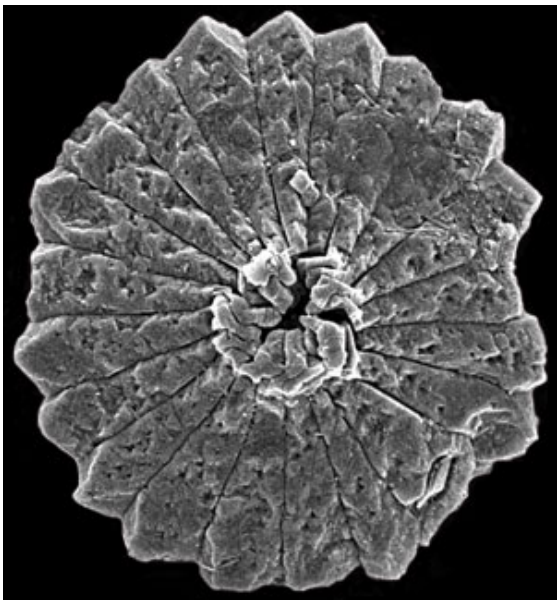


Figure 6: Calcium carbonate nanofossil before and during an OA event. Scanning electron micrograph (SEM) images of a calcareous nannofossil (Discoaster) (a) before and (b) during the Paleocene-Eocene Thermal Maximum, which was a period of ocean acidification in geological history. Images courtesy of P. Ziveri.





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Mail: Woods Hole Oceanographic Institution, 266 Woods Hole Road, Woods Hole, MA 02543, USA.
E-Contact: info@whoi.edu; press relations: media@whoi.edu, tel. (508) 457-2000
Problems or questions about the site, please contact webdev@whoi.edu