

# Anthropogenic carbon and ocean pH

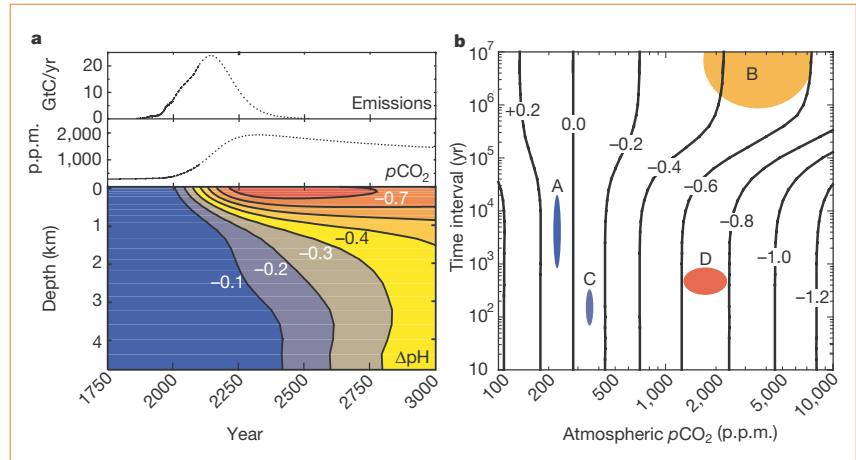
The coming centuries may see more ocean acidification than the past 300 million years.

Most carbon dioxide released into the atmosphere as a result of the burning of fossil fuels will eventually be absorbed by the ocean<sup>1</sup>, with potentially adverse consequences for marine biota<sup>2–4</sup>. Here we quantify the changes in ocean pH that may result from this continued release of CO<sub>2</sub> and compare these with pH changes estimated from geological and historical records. We find that oceanic absorption of CO<sub>2</sub> from fossil fuels may result in larger pH changes over the next several centuries than any inferred from the geological record of the past 300 million years, with the possible exception of those resulting from rare, extreme events such as bolide impacts or catastrophic methane hydrate degassing.

When carbon dioxide dissolves in the ocean it lowers the pH, making the ocean more acidic. Owing to a paucity of relevant observations, we have a limited understanding of the effects of pH reduction on marine biota. Coral reefs<sup>2</sup>, calcareous plankton<sup>3</sup> and other organisms whose skeletons or shells contain calcium carbonate may be particularly affected. Most biota reside near the surface, where the greatest pH change would be expected to occur, but deep-ocean biota may be more sensitive to pH changes<sup>4</sup>.

To investigate the effects of CO<sub>2</sub> emissions on ocean pH, we forced the Lawrence Livermore National Laboratory ocean general-circulation model<sup>5</sup> (Fig. 1a) with the pressure of atmospheric CO<sub>2</sub> (pCO<sub>2</sub>) observed from 1975 to 2000, and with CO<sub>2</sub> emissions from the Intergovernmental Panel on Climate Change's IS92a scenario<sup>1</sup> for 2000–2100. Beyond 2100, emissions follow a logistic function for the burning of the remaining fossil-fuel resources (assuming 5,270 gigatonnes of carbon (GtC) in 1750; refs 6, 7). Simulated atmospheric CO<sub>2</sub> exceeds 1,900 parts per million (p.p.m.) at around the year 2300. The maximum pH reduction at the ocean surface is 0.77; we estimate, using a geochemical model<sup>8,9</sup>, that changes in temperature, weathering and sedimentation would reduce this maximum reduction by less than 10%.

A review<sup>10</sup> of estimates of palaeo-atmospheric CO<sub>2</sub> levels from geochemical models, palaeosols, algae and forams, plant stomata and boron isotopes concluded that there is no evidence that concentrations were ever more than 7,500 p.p.m. or less than 100 p.p.m. during the past 300 million years (Myr). Moreover, the highest concentrations inferred from the geological record were thought to have developed over many millions of years owing to slow processes involving tectonics and biological evolution.



**Figure 1** Atmospheric release of CO<sub>2</sub> from the burning of fossil fuels may give rise to a marked increase in ocean acidity. **a**, Atmospheric CO<sub>2</sub> emissions, historical atmospheric CO<sub>2</sub> levels and predicted CO<sub>2</sub> concentrations from this emissions scenario, together with changes in ocean pH based on horizontally averaged chemistry. **b**, Estimated maximum change in surface ocean pH as a function of final atmospheric CO<sub>2</sub> pressure, and the transition time over which this CO<sub>2</sub> pressure is linearly approached from 280 p.p.m. A, glacial–interglacial CO<sub>2</sub> changes<sup>13</sup>; B, slow changes over the past 300 Myr; C, historical changes<sup>1</sup> in ocean surface waters; D, unabated fossil-fuel burning over the next few centuries.

We estimated the effect of past changes in atmospheric CO<sub>2</sub> levels on ocean pH by using a four-box ocean/atmosphere model<sup>8,9</sup>. Modelled processes include weathering of carbonate and silicate minerals on land, production of shallow-water carbonate minerals, production and oxidation of biogenic organic carbon, production and dissolution of biogenic carbonate minerals in the ocean, air–sea gas exchange of carbon, and transport by advection, mixing and biological processes.

In a series of simulations, atmospheric pCO<sub>2</sub> was varied linearly from the pre-industrial value (about 280 p.p.m.) to stabilization values from 100–10,000 p.p.m. over time intervals of 10–10<sup>7</sup> yr. For each simulation, we recorded the maximum predicted perturbation in pH in the surface-ocean boxes (Fig. 1b). When a CO<sub>2</sub> change occurs over a short time interval (that is, less than about 10<sup>4</sup> yr), ocean pH is relatively sensitive to added CO<sub>2</sub>. However, when a CO<sub>2</sub> change occurs over a long time interval (longer than about 10<sup>5</sup> yr), ocean chemistry is buffered by interactions with carbonate minerals, thereby reducing sensitivity to pH changes<sup>11</sup>.

Based on the record<sup>10</sup> of atmospheric CO<sub>2</sub> levels over the past 300 Myr and our geochemical model<sup>8,9</sup>, there is no evidence that ocean pH was more than 0.6 units lower than today. Our general circulation model results indicate that continued release of fossil-fuel CO<sub>2</sub> into the atmosphere could lead to a pH reduction of 0.7 units. We

conclude that unabated CO<sub>2</sub> emissions over the coming centuries may produce changes in ocean pH that are greater than any experienced in the past 300 Myr, with the possible exception of those resulting from rare, catastrophic events in Earth's history<sup>8,12</sup>.

**Ken Caldeira\***, **Michael E. Wickett†**

\*Energy and Environment Directorate and  
†Center for Applied Scientific Computing, Lawrence Livermore National Laboratory, 7000 East Avenue, Livermore, California 94550, USA  
e-mail: kenc@llnl.gov

- Houghton, J. T. et al. (eds) *Climate Change 2001: The Scientific Basis* (Contribution of Working Group I to the Third Assessment Report of the IPCC, Cambridge Univ. Press, Cambridge, 2001).
- Kleypas, J. A. et al. *Science* **284**, 118–120 (1999).
- Riebesell, U. et al. *Nature* **407**, 364–367 (2000).
- Seibel, B. A. & Walsh, P. J. *Science* **294**, 319–320 (2001).
- Caldeira, K. & Duffy, P. B. *Science* **287**, 620–622 (2000).
- Metz, B., Davidson, O., Swart, R. & Pan, J. (eds) *Climate Change 2001: Mitigation* (Contribution of Working Group III to the Third Assessment Report of the IPCC, Cambridge Univ. Press, Cambridge, 2001).
- Marland, G., Boden, T. A. & Andres, R. J. Global, regional, and national CO<sub>2</sub> emissions. *Trends: A Compendium of Data on Global Change* [http://cdiac.esd.ornl.gov/trends/emis/tre\\_glob.htm](http://cdiac.esd.ornl.gov/trends/emis/tre_glob.htm) (2002).
- Caldeira, K. & Rampino, M. R. *Paleoceanography* **8**, 515–525 (1993).
- Caldeira, K. & Rau, G. H. *Geophys. Res. Lett.* **27**, 225–228 (2000).
- Crowley, T. J. & Berner, R. A. *Science* **292**, 780–781 (2001).
- Caldeira, K., Berner, R., Sundquist, E. T., Pearson, P. N. & Palmer, M. R. *Science* **286**, 2043 (1999).
- Beerling, D. J. & Berner, R. A. *Global Biogeochem. Cycles* **16**, 101–113 (2002).
- Sanyal, A., Hemming, N. G., Hanson, G. N. & Broecker, W. S. *Nature* **373**, 234–236 (1995).

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