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## Anthropogenic carbon and ocean pH

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Most fossil-fuel CO<sub>2</sub> released to the atmosphere will eventually be absorbed by the ocean<sup>1</sup> with potentially adverse consequences for marine biota<sup>2-4</sup>. We quantify pH changes that may result from continued release of fossil-fuel CO<sub>2</sub> to the atmosphere, and compare these with pH changes inferred from geological and historical records. We conclude that releasing fossil-fuel CO<sub>2</sub> to the atmosphere over several centuries may result in ocean pH changes greater than any inferred from the geologic record of the past 300 million years, with the possible exception of rare extreme events such as bolide impacts or catastrophic methane hydrate degassing.

When carbon dioxide dissolves in the ocean it increases the hydrogen-ion concentration, lowering ocean pH (i.e., negative common log of the hydrogen ion activity). Due to a paucity of relevant observations, we have a limited understanding of the effects of pH reductions on marine biota. Coral reefs<sup>2</sup>, calcareous plankton<sup>3</sup>, and other organisms with calcium carbonate skeletal material or shells may be particularly impacted by decreased ocean pH. Most biota resides primarily near the surface where greatest pH change can be expected to occur, but deep ocean biota may be more sensitive to pH changes<sup>4</sup>.

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To study effects of CO<sub>2</sub> emissions on ocean pH, we forced the LLNL ocean general circulation model<sup>5</sup> with observed atmospheric pCO<sub>2</sub> from 1975 to 2000 and with CO<sub>2</sub> emissions from the IPCC IS92a scenario<sup>1</sup> from year 2000 to 2100. Beyond 2100, emissions from burning fossil fuel resources (F) are described with a logistic function (Fig. 1) implying fossil fuel resources<sup>6</sup> of 5000 GtC in year 2000. Maximum simulated atmospheric CO<sub>2</sub> concentration is exceeds 1900 ppm near year 2300. Maximum ocean pH decrease is 0.77 near the surface (Fig. 1), based on horizontally averaged ocean chemistry. We estimate, using the geochemical model<sup>7,8</sup> described below, that consideration of changes in temperature, weathering, and sedimentation would reduce this maximum decrease by <10%.

A review<sup>9</sup> of estimates of paleo-atmospheric CO<sub>2</sub> concentration from geochemical models, paleosols, algae and forams, plant stomata, and boron isotopes concluded that there is no evidence that concentrations exceeded 7,500 ppm or were less than 100 ppm over the past 300 myr. In addition, the highest concentrations inferred from the geologic record were thought to have developed over many millions of years as a result of slow processes involving tectonics and biological evolution. On these time scales, ocean chemistry is buffered by interaction with carbonate minerals<sup>10</sup>.

We estimated the effect of these past changes in atmospheric CO<sub>2</sub> on ocean pH with a simple three-box ocean model embedded in a model of the long term carbonate-silicate cycle<sup>7,8</sup>. Modeled 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 biology.

In a series of simulations, atmospheric pCO<sub>2</sub> was increased linearly from the preindustrial value (~280 ppm) to a stabilization value ranging from 100 ppm to 10,000 ppm

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over time intervals ranging from 10 yr to  $10^7$  yr. For each model simulation, we recorded maximum predicted pH perturbation in for the surface ocean boxes (Fig. 2). If it occurs over several hundred thousand years or more, an increase in atmospheric  $CO_2$  to 7,500 ppm decreases ocean pH by ~0.6 units.

Based on the record<sup>9</sup> of atmospheric CO<sub>2</sub> over the past 300 myr and our geochemical model<sup>7,8</sup>, we conclude that there is no evidence that ocean pH was more than 0.6 units lower than today. Our GCM results indicate that continued fossil-fuel burning with atmospheric CO<sub>2</sub> release could lead to pH decreases of ~0.7 units. Thus, we conclude that unabated CO<sub>2</sub> emissions over the next several hundred years may produce changes in ocean pH greater in magnitude than any experienced in the past 300 myr, with the possible exception of rare catastrophic events in Earth history<sup>7,11</sup>.

### References

- 1 Houghton J T et al. (eds), Climate Change 2001 the scientific basis. Contribution of Working Group I to the Third Assessment Report of the Intergovernmental Panel on Climate Change. Cambridge University Press, 944 pp, (2001).
- 2. Kleypas, J. A. et al. Geochemical consequences of increased atmospheric carbon dioxide on coral reefs. *Science* 284, 118–120 (1999).
- 3. Riebesell, U. *et al.* Reduced calcification of marine plankton in response to increased atmospheric CO<sub>2</sub>. *Nature* **407**, 364–367 (2000).
- 4. Seibel, B. A. & Walsh, P. J. Carbon cycle Potential impacts of CO<sub>2</sub> injection on deep-sea biota. *Science* **294**, 319–320 (2001).
- 5. Caldeira, K. & Duffy, P. B. The role of the Southern Ocean in uptake and storage of anthropogenic carbon dioxide. *Science* **287**, 620–622 (2000).

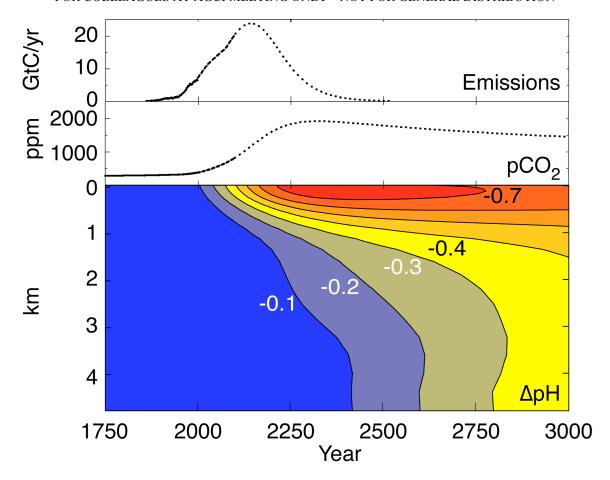
#### FOR COLLEAGUES AT AGCI MEETING ONLY --NOT FOR GENERAL DISTRIBUTION

- 6. 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 Intergovernmental Panel on Climate Change. Cambridge University Press, 700 pp. (2001).
- 7. Caldeira, K. & Rampino, M. R. Aftermath of the end-Cretaceous mass extinction possible biogeochemical stabilization of the carbon cycle and climate. *Paleoceanography* **8**, 515–525 (1993).
- 8. Caldeira, K. & Rau, G. H. Accelerating carbonate dissolution to sequester carbon dioxide in the ocean: Geochemical implications. *Geophys. Res. Letters* **27**, 225–228 (2000).
- 9. Crowley, T. J. & Berner, R. A. Paleoclimate CO<sub>2</sub> and climate change. *Science* **292**, 780–781 (2001).
- 10. Caldeira, K. & Berner, R. Seawater pH and atmospheric carbon dioxide (Technical comment) *Science* **286**, 2043a (1999).
- 11. Beerling, D. J. & Berner, R. A. Biogeochemical constraints on the Triassic-Jurassic boundary carbon cycle event. *Global Biogeochem. Cycles* **16**, 101–113 (2002).
- 12. Sanyal, A., Hemming, N. G., Hanson, G. N. & Broecker, W. S. Evidence for a higher pH in the glacial ocean from boron isotopes in foraminifera. *Nature* **373**, 234–236 (1995).
- 13. Marland, G., Boden, T.A. & Andres, R.J. Global, Regional, and National Fossil Fuel CO<sub>2</sub> Emissions. In Trends: A Compendium of Data on Global Change. Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U.S. Department of Energy, Oak Ridge, Tenn., U.S.A (2002).

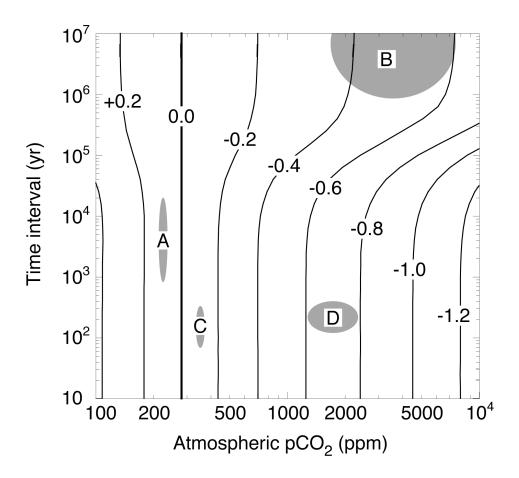
**Acknowledgements** This research was supported by the DOE Office of Science Office of Biological and Environmental Research Ocean Carbon Sequestration Research Program. This work was performed under

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the auspices of the U.S. Department of Energy by University of California Lawrence Livermore National Laboratory under contract No. W-7405-Eng-48.



**Figure 1. (top)** Historical CO<sub>2</sub> emissions <sup>13</sup> to year 2000, IS92a CO<sub>2</sub> emissions to year 2100, and emissions after 2100 burning remaining fossil fuels <sup>6</sup> according to the logistic formula, dF/dt = (-2.92 x 10<sup>5</sup> GtC yr)<sup>-1</sup> F(t) [(5270 GtC) - F(t)]. (center) Historical atmospheric CO<sub>2</sub> and CO<sub>2</sub> predicted from this emissions scenario. CO<sub>2</sub> levels rise from the pre-industrial value of 280 ppm to a maximum of >1900 ppm near year 2300. (bottom) Horizontally averaged ocean pH is predicted to decrease by more than 0.7 units near the surface. By the end of the millennium, deep-ocean pH is reduced more than 0.3 units.



**Figure 2.** Estimated maximum surface ocean pH change as a function of final atmospheric pCO<sub>2</sub> and the transition time in which this pCO<sub>2</sub> is linearly approached from an initial "pre-industrial" condition of 280 ppm: (A) glacial-interglacial CO<sub>2</sub> changes<sup>12</sup>, (B) long-term changes<sup>9</sup> 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. When a CO<sub>2</sub> change occurs over a short time interval (i.e.,  $< \sim 10^4$  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 (i.e.,  $> \sim 10^5$  yr), ocean chemistry is buffered by interactions with carbonate minerals, lowering pH sensitivity <sup>7</sup>.

Caldeira and Wickett