Anthropogenic carbon and ocean pH

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Most fossil-fuel CO_2 released to the atmosphere will eventually be absorbed by the ocean[1] with potentially adverse consequences for marine biota[2–4]. We quantify pH changes that may result from continued release of fossil-fuel CO_2 to the atmosphere, and compare these with pH changes estimated from geological and historical records. We conclude that releasing fossil-fuel CO_2 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 lowers the pH, making the ocean more acidic. Due to a paucity of relevant observations, we have a limited understanding of the effects of pH reductions on marine biota. Coral reefs[2], calcareous plankton[3], and other organisms with calcium carbonate skeletal material or shells may be particularly impacted. Most biota resides near the surface where greatest pH change can be expected to occur, but deep ocean biota may be more sensitive to pH changes[4].

To study effects of CO_2 emissions on ocean pH, we forced the LLNL ocean general circulation model[5] (Fig. 1a) with observed atmospheric pCO_2 from 1975 to 2000 and with CO_2 emissions from the IPCC IS92a scenario[1] from year 2000 to 2100. Beyond 2100, emissions follow a logistic function burning remaining fossil fuel resources (assuming 5270 GtC in year 1750; ref. 6, 7). Simulated atmospheric CO_2 exceeds 1900 ppm near

year 2300. Maximum surface ocean pH decrease is 0.77 . We estimate, using the geochemical model[8,9] described below, that changes in temperature, weathering, and sedimentation would reduce this maximum decrease by <10%.

A review[10] of estimates of paleo-atmospheric CO_2 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 due to slow processes involving tectonics and biological evolution.

We estimated the effect of past changes in atmospheric CO_2 on ocean pH with a four-box ocean/atmosphere model[8,9]. 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_2 was varied linearly from the pre-industrial value (~280 ppm) to stabilization values ranging from 100 ppm to 10,000 ppm over time intervals ranging from 10 yr to 10^7 yr. For each model simulation, we recorded maximum predicted pH perturbation in the surface ocean boxes (Fig. 1b). When a CO_2 change occurs over a short time interval (i.e., $< \sim 10^4$ yr), ocean pH is relatively sensitive to added CO_2. However, when a CO_2 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 [11].

Based on the record[10] of atmospheric CO_2 over the past 300 myr and our geochemical model[8,9], 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_2 release could lead to pH decreases of 0.7 units. Thus, we conclude that unabated

CO_2 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[8,12].

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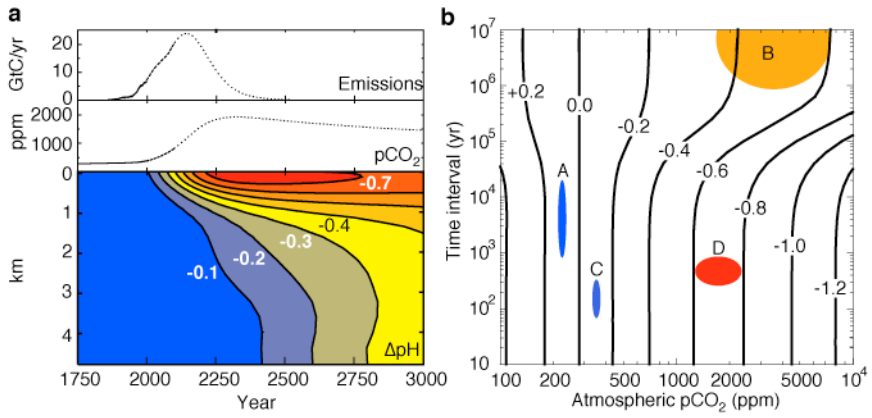

Figure 1 Atmospheric release of fossil fuel CO_2 may make the ocean more acid than it has been for the past 300 myr. **a,** Atmospheric CO_2 emissions, historical atmospheric CO_2 and CO_2 predicted from this emissions scenario, and change in ocean pH based on horizontally averaged chemistry. **b,** Estimated maximum surface ocean pH change as a function of final atmospheric pCO_2 and the transition time over which this pCO_2 is linearly approached from 280 ppm: A, glacial-interglacial CO_2 changes[13]; B, slow changes over the past 300 myr; C, historical changes[1] in ocean surface waters; D, unabated fossil-fuel burning over the next few centuries.