Such ion gels have shown superior performance as gate dielectrics in organic thin-film transistors (*5*). For many organic semiconductors, device performance is constrained by the number of charge carriers rather than their mobility; the high capacitance of the ion gel boosts the carrier density in the semiconductor channel. Further, the high ionic mobility enables switching speeds that are orders of magnitude higher than with conventional polymer electrolytes (*6*).

Similar ion gels could form the basis of electromechanical actuators (*7*, *8*); differential ion migration in response to an applied electric field leads to differential gel swelling and thus to bending. A possible route to accentuate this effect would be to polymerize the cations into the B blocks, thus immobilizing some or all of that charge (*9*, *10*); the much more mobile anions could then generate a highly asymmetric swelling.

The same molecular architecture also holds promise for gas separation. Ionic liquids strongly prefer to dissolve CO_2 and SO_2 over, for example, N_2 and CH_4. Because transport through an ionic liquid is so facile, it is possible to achieve combinations of selectivity and throughput comparable to those of the best materials currently available. However, a functional gas separation membrane must withstand a substantial pressure drop. The ionic liquid could be literally blown out of the simple ion gel. A polymerized ion gel should not suffer from this drawback, because the attraction between ions would far outweigh the external pressure. Direct polymerization of organic cations has recently been achieved (*9*, *10*). By incorporating an appropriate difunctional monomer, Bara *et al.* have prepared and evaluated cross-linked films for the separation of CO_2 from CH_4 or N_2 (*9*), with promising results.

Applications to other technologies such as fuel cell membranes and lithium battery separators often require much greater mechanical rigidity and high-temperature stability while retaining high ionic mobility along a given axis. Here, the ability of block polymers to self-assemble into well-defined nanostructures with long-range order holds the key (*11*). For example, macroscopic orientation of block polymer cylinders has been achieved by various strategies, including application of flow fields and electric fields and by preparation of suitably treated underlying substrates (see the second figure, top panel) . However, it
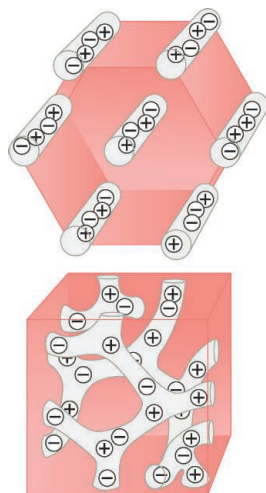
Self-assembly. Block polymers can self-assemble into (**top**) hexagonally packed cylinders or (**bottom**) the double gyroid. The ionic liquid is confined to the white channels, whereas the red matrix consists of the insoluble block.

remains difficult to achieve macroscopic orientation and perfection of the resulting membrane, which is important for some applications. Alternatively, a network structure such as the double gyroid is isotropic, obviating the need for orientation (see the second figure, bottom panel). Unfortunately, this structure can only be achieved under limited combinations of copolymer compositions, molar masses, and processing conditions. Use of multiblock polymers, such as ABC terpolymers, allows network materials to be prepared over much wider ranges of molecular variables and with greatly enhanced mechanical strength (*12*).

Recent progress in the development of controlled polymerization has enabled the synthesis of almost any desired architecture, with almost unlimited choice of monomers, such that tailored multiblock polymers can be readily produced. The outstanding challenges are to design block polymer–ionic liquid composite materials with desired combinations of mechanical integrity, controlled nanostructure, and ionic liquid properties. This class of materials is only beginning to be explored and many design rules are yet to be mapped out in detail, but rapid progress can be expected because related polymer-based technologies are well established.

References
1. T. Ueki, M. Watanabe, *Macromolecules* **41**, 3739 (2008).
2. M. A. B. H. Susan, T. Kaneko, A. Noda, M. Watanabe, *J. Am. Chem. Soc.* **127**, 4976 (2005).
3. Y. He, P. G. Boswell, P. Bühlmann, T. P. Lodge, *J. Phys. Chem. B* **111**, 4645 (2007).
4. Y. He, T. P. Lodge, *Macromolecules* **41**, 167 (2008).
5. J. Lee, M. J. Panzer, Y. He, T. P. Lodge, C. D. Frisbie, *J. Am. Chem. Soc.* **129**, 4532 (2007).
6. J. H. Cho et al., *Adv. Mater.* **20**, 686 (2008).
7. W. Lu et al., *Science* **297**, 983 (2002).
8. J. Ding et al., *Chem. Mater.* **15**, 2392 (2003).
9. J. E. Bara et al., *Ind. Eng. Chem.* **46**, 5397 (2007).
10. J. Tang et al., *Chem. Commun.* **2005**, 3325 (2005).
11. P. M. Simone, T. P. Lodge, *Macromolecules* **41**, 1753 (2008).
12. T. H. Epps III et al., *Macromolecules* **37**, 7085 (2004).

10.1126/science.1159652

OCEANS

Carbon Emissions and Acidification

Richard E. Zeebe¹*, **James C. Zachos,²** **Ken Caldeira,³** **Toby Tyrrell⁴**

Avoiding environmental damage from ocean acidification requires reductions in carbon dioxide emissions regardless of climate change.

Much of the scientific and public focus on anthropogenic carbon dioxide (CO_2) emissions has been on climate impacts. Emission targets have been suggested based primarily on arguments for preventing climate from shifting significantly from its preindustrial state. However, recent studies underline a second major impact of carbon emissions: ocean acidification. Over the past 200 years, the oceans have taken up ~40% of the anthropogenic CO_2 emissions. This uptake slows the rise in atmospheric CO_2 considerably, thus alleviating climate change caused by anthropogenic greenhouse gas emissions. But it also alters ocean chemistry, with potentially serious consequences for marine life (*1*).

Oceanic uptake of anthropogenic CO_2 leads to a decrease in seawater pH and thus lowers the saturation state for carbonate minerals such as calcite and aragonite ($CaCO_3$). This process, termed ocean acidification, is expected to have detrimental consequences for a variety of marine organisms (*2*, *3*). For example, a decline in carbonate saturation state will affect the stability and likely production rates of $CaCO_3$ minerals, which are the building blocks of coral reefs and form the shells and skeletons of other marine calcifying species. Independent of climatic considerations, carbon emissions must be reduced to avoid these consequences.

¹Department of Oceanography, University of Hawaii, Honolulu, HI 96822, USA. ²Earth and Planetary Sciences Department, University of California at Santa Cruz, Santa Cruz, CA 95060, USA. ³Department of Global Ecology, Carnegie Institution, Stanford, CA 94305, USA. ⁴National Oceanography Centre, Southampton University, Southampton, SO14 3ZH, UK. *To whom correspondence should be addressed. E-mail: zeebe@soest.hawaii.edu

The range of tolerable pH changes (where "tolerable" means "without substantial detriment to organism fitness") is as yet unknown for many marine organisms. In laboratory and mesocosm studies, a decrease of 0.2 to 0.3 units in seawater pH inhibits or slows calcification in many marine organisms, including corals (*4*), foraminifera (*5*), and some calcareous plankton (*6, 7*). A drop of 0.3 pH units corresponds to a doubling of the hydrogen ion concentration [H^+], because pH is expressed on a logarithmic scale as pH = $-\log([H^+])$.

Compared with preindustrial levels, average surface ocean pH has already decreased by ~0.1 units (*2*). If future increases in seawater acidity affect calcification in coral reefs, such that erosion outweighs accretion, then the reefs could lose structural stability, with further negative implications for reef communities and for shore protection (*3*). Reduced calcification in shellfish such as oysters and mussels would impact worldwide commercial aquaculture production (*8*). Effects of ocean acidification on noncalcifying organisms such as viruses and bacteria are largely unknown, as are potential consequences for marine food webs.

Thus, although the response of different organisms is expected to be inhomogeneous (*9*), current evidence suggests that large and rapid changes in ocean pH will have adverse effects on a number of marine organisms. Yet, environmental standards for tolerable pH changes have not been updated in decades. For example, the seawater quality criteria of the U.S. Environmental Protection Agency date back to 1976 and state that for marine aquatic life, pH should not be changed by more than 0.2 units outside of the normally occurring range (*10*). These standards must be reevaluated based on the latest research on pH effects on marine organisms. Once new ranges of tolerable pH are adopted, CO_2 emission targets must be established to meet those requirements in terms of future seawater chemistry changes.

The key variables that will determine the extent of future seawater chemistry changes—and therefore the impact on marine life—is the magnitude and time scale of the anthropogenic carbon release. For specific CO_2 emission scenarios, changes in atmospheric CO_2, surface ocean pH, and carbonate mineral saturation state have been calculated with different carbon cycle models (*1, 11–*
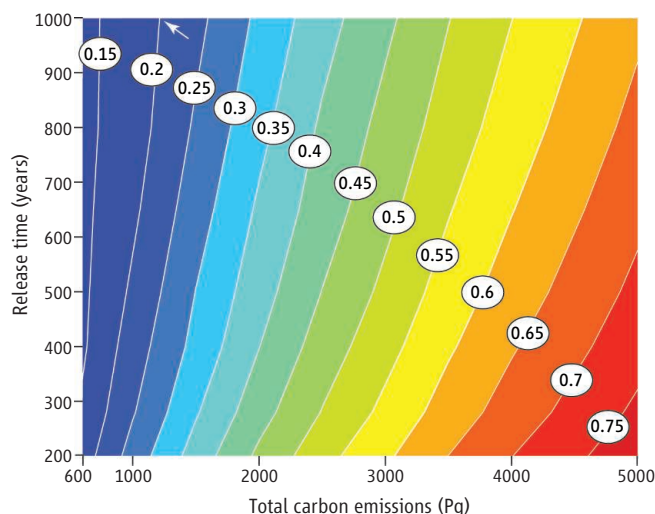
Surface ocean pH decline. The white contour lines illustrate the expected maximum pH decrease of average surface ocean waters in the future (in pH units) as a function of total anthropogenic CO_2 emissions (in petagrams of carbon, 1 Pg = 10^{15} g) and release time (in years, see supporting online material). For example, if humans release a total of 1200 Pg C over 1000 years, surface ocean pH will drop by about 0.2 units (arrow).

13). Fortunately, and in contrast to climate model predictions, such future ocean chemistry projections are largely model-independent on a time scale of a few centuries, mainly because the chemistry of CO_2 in seawater is well known (*14*) and changes in surface ocean carbonate chemistry closely track changes in atmospheric CO_2. Predicted changes in surface ocean pH for given total emissions and release time of anthropogenic carbon are thus similar among different types of models over the next few centuries [see supporting online material and (*1, 11–13*)].

Projected changes in ocean carbonate chemistry should serve as a guideline for policy protocols that identify CO_2 emission targets to reduce the effects of human-made ocean acidification. For example, to avoid a surface ocean pH decline by more than 0.2 units (*10*), total emission targets would have to range from ~700 Pg C over 200 years to ~1200 Pg C over 1000 years (see the figure). Such scenarios would be difficult to achieve, however, because they require immediate reductions in global emissions. If emissions can be reduced after the year 2050 and capped at 1500 Pg C, surface ocean pH would decline by ~0.35 units relative to preindustrial levels. The aragonite saturation state in the warm surface ocean would drop from ~3.5 to ~2.1 under this scenario (see supporting online material). Substantial reductions in coral calcification have been reported over this range (*2–4*).

Predictions of changes in calcification rates and other physiological responses in marine organisms to ocean acidification are hampered by a lack of adequate experimental

data and field observations. Most studies indicate reduced calcification rates at high CO_2 (*2–8, 11*), but some find little change or increasing cellular calcification rates (*9, 15*). The key is to understand the response of the functional groups that drive marine biogeochemical cycles. For instance, very few studies have examined foraminifera (*5*), which are major contributors to the production and deposition of calcium carbonate in the ocean. Also, long-term experiments are necessary with different calcifying and non-calcifying groups to test their ability to adapt to a high–CO_2 world.

To monitor and quantify future changes in ocean chemistry and biogeochemical fluxes, intensified global-ocean carbon dioxide surveys in combination with carbon-cycle modeling will be necessary. Awareness must be raised among the public and policy-makers of the effects of ocean acidification and the steps required to control it. Ocean chemistry changes, and not only climate effects, should be taken into consideration when determining CO_2 emission targets; such consideration is likely to weigh in favor of lower emission targets.

References
1. K. Caldeira, M. E. Wickett, *Nature* **425**, 365 (2003).
2. J. Raven *et al.*, *Ocean Acidification Due to Increasing Atmospheric Carbon Dioxide* (The Royal Society, Policy Document, London, UK, 2005).
3. O. Hoegh-Guldberg *et al.*, *Science* **318**, 1737 (2007).
4. J. A. Kleypas *et al.*, *Science* **284**, 118 (1999).
5. J. Bijma, H. J. Spero, D. W. Lea, *Use of Proxies in Paleoceanography: Examples from the South Atlantic*, G. Fischer, G. Wefer, Eds. (Springer, Berlin, 1999), pp. 489–512.
6. D. A. Wolf-Gladrow, U. Riebesell, S. Burkhardt, J. Bijma, *Tellus* B **51**, 461 (1999).
7. U. Riebesell *et al.*, *Nature* **407**, 364 (2000).
8. F. Gazeau, C. Quiblier, J. M. Jansen, J.-P. Gatusso, *Geophys. Res. Lett.* **34**, L07603 (2007).
9. G. Langer *et al.*, *Geochem. Geophys. Geosyst.* **7**, Q09006 (2006).
10. U.S. Environmental Protection Agency, *Quality Criteria for Water* (Washington, DC, 1976).
11. J. C. Orr *et al.*, *Nature* **437**, 681 (2005).
12. A. Montenegro, V. Brovkin, M. Eby, D. Archer, A. J. Weaver, *Geophys. Res. Lett.* **34**, L19707 (2007).
13. J. C. Zachos, G. R. Dickens, R. E. Zeebe, *Nature* **451**, 279 (2008).
14. R. E. Zeebe, D. A. Wolf-Gladrow, *CO_2 in Seawater: Equilibrium, Kinetics, Isotopes* (Elsevier Oceanography Series, Amsterdam, 2001).
15. M. D. Iglesias-Rodriguez *et al.*, *Science* **320**, 336 (2008).
16. This work was supported by NSF grant NSFOCE07-51959 to R.E.Z.