nature geoscience

LETTERS

PUBLISHED ONLINE: 14 FEBRUARY 2010 | DOI: 10.1038/NGEO755

Past constraints on the vulnerability of marine calcifiers to massive carbon dioxide release

Andy Ridgwell[1]* and Daniela N. Schmidt[2]

Increasing concentrations of carbon dioxide in sea water are driving a progressive acidification of the ocean[1]. Although the associated changes in the carbonate chemistry of surface and deep waters may adversely affect marine calcifying organisms[2–4], current experiments do not always produce consistent results for a given species[5]. Ocean sediments record past biological responses to transient greenhouse warming and ocean acidification. During the Palaeocene–Eocene thermal maximum, for example, the biodiversity of benthic calcifying organisms decreased markedly[6,7], whereas extinctions of surface dwellers were very limited[8,9]. Here we use the Earth system model GENIE-1 to simulate and compare directly past and present environmental changes in the marine realm. In our simulation of future ocean conditions, we find an undersaturation with respect to carbonate in the deep ocean that exceeds that experienced during the Palaeocene–Eocene thermal maximum and could endanger calcifying organisms. Furthermore, our simulations show higher rates of environmental change at the surface for the future than the Palaeocene–Eocene thermal maximum, which could potentially challenge the ability of plankton to adapt.

Calcifying marine organisms may be adversely affected by future ocean acidification if declining carbonate saturation influences their ability to produce shells and skeletons out of calcium carbonate[2–4] ($CaCO_3$). Although the reaction of calcifying organisms to simulated future ocean acidification has been extensively tested under laboratory conditions, responses seem highly species specific[2] and the impact on ecosystems in the open ocean may be qualitatively rather different[5]. Furthermore, species may be able to physiologically evolve through genetic change or adapt through shifts in biogeography, neither of which can be quantified experimentally in the laboratory owing to the spatiotemporal scales over which these phenomena occur in the natural world. Hence, the best current possibility to test for ecosystem response and adaptation potential to transient warming and ocean acidification is by interrogating the geological record.

Marine organisms have experienced substantial secular variability in their environment over geological timescales (Fig. 1). Surface pH conditions may have been ~0.6–0.7 pH units lower during the Cretaceous and Jurassic periods compared with modern conditions, yet calcareous plankton originated, diversified and proliferated during these periods (Fig. 1a). However, long-term quasi-steady-state conditions of low pH do not necessarily imply a crisis for planktic carbonate production for two main reasons. First, on million-year (tectonic) timescales, individuals and ecosystems will adapt and evolve to changing climate and ocean geochemistry. Second, carbonate saturation (Ω) determines the stability of the common biogenic carbonate minerals (calcite and aragonite) and hence controls $CaCO_3$ preservation and burial globally. Ocean carbonate saturation is thus generally well regulated by the simple requirement that on 'long' (>10 kyr) timescales, sources (weathering) and sinks (shallow- and deep-water $CaCO_3$ burial) must balance[10]. In contrast, as pH reflects the balance between dissolved CO_2 ($CO_{2(aq)}$) and carbonate ion (CO_3^{2-}) concentrations, it is governed primarily by pCO_2 (controlling [$CO_{2(aq)}$] for given temperature) and Ca^{2+}/Mg^{2+} (controlling [CO_3^{2-}] for given Ω) rather than weathering. Hence, there was no late Mesozoic carbonate crisis because Ω was maintained relatively high and decoupled from pH (ref. 10; Fig. 1).

Only events involving geologically 'rapid' (<10 kyr) CO_2 release will overwhelm the ability of the ocean and sediments to regulate Ω, producing a coupled decline in both pH and saturation state and hence providing a future-relevant test of ocean acidification impacts. We focus on the Palaeocene–Eocene thermal maximum (PETM) 55.5 million years ago (Myr): an event characterized by a transient climatic warming and associated with clear isotopic and carbonate dissolution evidence for a massive release of carbon[6,11]. Critically, the geological record provides information regarding the response of marine calcifiers to the ensuing warming and acidification. Observations document a migration of warm-water planktic taxa towards higher latitudes and increased evolutionary turnover in both calcareous phytoplankton[8] and zooplankton[9], but no net extinction in either plankton group. Furthermore, ocean acidification during the PETM did not impart a bias in extinction or diversification towards less calcifying planktic species[8]. This observation does not imply a lack of detrimental impacts in the future because rates of environmental change are generally assumed faster than at the PETM (for example, ref. 8). However, explicit assessment of modern versus Palaeocene–Eocene ocean acidification is lacking. This is important because the past sensitivity of ocean circulation and carbon cycling to CO_2 release and greenhouse warming will not necessarily be the same as now[12].

We address this question using an Earth system model—GENIE-1 (see Methods). We start with the model configured for the present day and test a range of possible acidification futures. We use the same model for the PETM but account for differences in initial Palaeocene climate and carbon cycling (see the Methods section), following a similar methodology to ref. 13. The steady-state conditions predicted by the two different model configurations closely agree with available reconstructions of past ocean-surface pH (Fig. 1b) and support a late Palaeocene ocean surface that was about 0.4 pH units lower than today. For the modern, we focus on the consequences of the IS92a emissions scenario[14] followed by a linear reduction in emissions after year 2100 to give a total carbon release of 2,180 PgC. We chose this amount of total fossil-fuel 'burn' for convenience in making comparison with estimated PETM release (assuming a biogenic methane source[13]). However, estimates of fossil-fuel resources exceed this total by a factor

[1]School of Geographical Sciences, University of Bristol, University Road, Bristol BS8 1SS, UK, [2]Department of Earth Sciences, University of Bristol, Bristol BS8 1RJ, UK. *e-mail: andy@seao2.org.

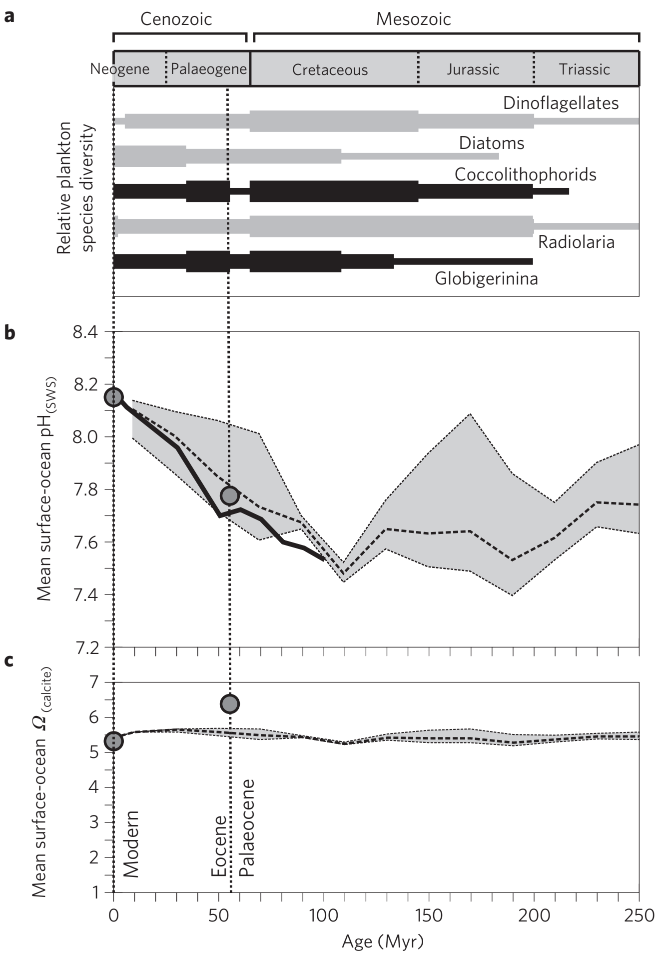

Figure 1 | The geological context for future ocean acidification. a, The evolutionary history of major calcifying (black) and non-calcifying (grey) taxa re-drawn from ref. 27. **b**, Available reconstructions of mean surface-ocean pH (seawater scale, 'pH_{SWS}'). The black dashed line is the mean model reconstruction of ref. 10 (the grey band delineates the minimum and maximum estimates); the solid black line is from ref. 28. The circles represent the predictions of the paired Earth-system model reconstructions presented here. **c**, The surface calcite saturation ($\Omega_{(calcite)}$, defined: $\Omega = [CO_3{}^{2-}][Ca^{2+}]/K$, where K is a stability constant and $[CO_3{}^{2-}]$ and $[Ca^{2+}]$ are the ambient carbonate and calcium ion concentrations, respectively) reconstructions of ref. 10 (black dashed line) and this study (circles). The grey band delineates how the same assumed range in palaeo atmospheric pCO_2 uncertainity as in **a** affects the saturation estimate. Vertical dotted line represents the Palaeocene–Eocene boundary.

of ~2 (ref. 1), hence making our future versus past assessment conservative. For the PETM, we have tested a carbon release judged to give the best fit to the palaeooceanographic record by ref. 13 (6,840 PgC over 10 kyr) as well as a smaller and faster release (2,180 PgC over 1 kyr) more similar to the analysis of ref. 15. (The results of other emissions scenarios we have tested are given in the Supplementary Information.)

We find that in the future, the calcite saturation horizon (where $\Omega = 1$ and below which calcite starts to dissolve) shoals rapidly to a depth of only about 600 m following the peak in atmospheric CO_2 around year 2150 (Fig. 2a). If only ocean–atmosphere equilibrium was important, extensive undersaturation and an acidification of over 0.3 pH units would persist indefinitely throughout the intermediate-to-deep ocean (Supplementary Fig. S3). However, dissolution of $CaCO_3$ in the surface sediments neutralizes some of the excess acidity and replenishes the carbonate ion inventory. Reduced global $CaCO_3$ burial compared with weathering results in a further increase of ocean alkalinity such that after 10 kyr, the saturation horizon has approached within 1 km of its pre-industrial position (Fig. 2a). Silicate weathering feedback[16], not accounted for in these experiments, is required to eventually fully restore ocean chemistry.

For the PETM, the decline in carbonate saturation is much less pronounced (Fig. 2b,c) and only when releasing 6,840 PgC does surface-ocean Ω fall by an amount comparable to our future predictions. More importantly, PETM surface Ω declines around an order of magnitude slower than in the future scenario. Greater silicate weathering rates, which have relatively little impact on 100–1,000 yr timescales[16], are sufficiently strong in the GENIE-1 model to raise mean surface Ω by almost one saturation unit after 10 kyr (not shown). Inclusion of this feedback would further enhance our predicted future versus PETM contrast owing to the differences in CO_2 release timescale. It should be noted that a rate of PETM CO_2 release more comparable to anthropogenic input today (that is, within a few hundred years) cannot be entirely ruled out sedimentologically. However, a plausible natural mechanism and source for such a rapid and large release is difficult to imagine. Furthermore, model analyses of the recorded shape of the event have all concluded a duration rather longer than 1 kyr and approaching 10 kyr (refs 13, 15). As species adaptation potential to environmental change will depend on the number of generations in a given time and the accumulated genetic variation[17], the faster future rate of surface environmental change will create a more severe adaptive pressure than that during the PETM (ref. 8). Whether future extinctions will result cannot be determined with any certainty at present.

In contrast to planktic organisms such as coccolithophores and foraminifers, which have, respectively, bi-weekly to monthly reproduction cycles, benthic foraminifers live several years, making the latter more vulnerable to environmental change[17]. Ecosystems of the deep sea are also among the most stable on Earth. This condition favours the evolution of specialists with narrow tolerance limits[18], whose narrow niche/specific adaptation constrains their ability to subsequently occupy alternative niches[19]. As a result, these organisms will be more susceptible to extinction compared with organisms adapted to highly variable (for example, surface ocean) environments. Deep-sea benthic foraminifers experienced a major extinction during the PETM (refs 6, 7). Hence, comparable rates and/or magnitudes of past and future environmental change would suggest a similar likelihood of extinction in the future.

For the benthic environment, we find that the initial future and Palaeocene–Eocene deep-sea responses to CO_2 release are consistent: with progressive decreases in pH (Fig. 3b), saturation state (Fig. 3c) and dissolved oxygen concentrations (Fig. 3e), while temperature increases (Fig. 3d). However, in the future experiment, deep-ocean O_2 and temperature rapidly recover and O_2 overshoots preindustrial conditions, while PETM conditions continue to deteriorate for thousands of years and recover only slowly thereafter. The recovery of benthic environmental conditions after the end of the current millennia is accelerated by a 'flushing' event—a behaviour observed on a multi-millennial timescale in other Earth-system models under both steady radiative[20] and transient[16] forcing. In this phenomenon, warming of the deep ocean creates unstable stratification with respect to Southern Ocean surface conditions, which then breaks down; ventilating the deep ocean. In contrast, the phenomenon does not occur in the Palaeogene simulation because the absence of seasonal sea ice allows surface-ocean temperatures at high southern latitudes to track the deep ocean through the warming transient, preventing the development of unstable stratification. Box models that run for similarly long experiments do not show such a phenomenon[21], reflecting their reduced spatial resolution and dynamics, whereas fully coupled general circulation models cannot generally be run

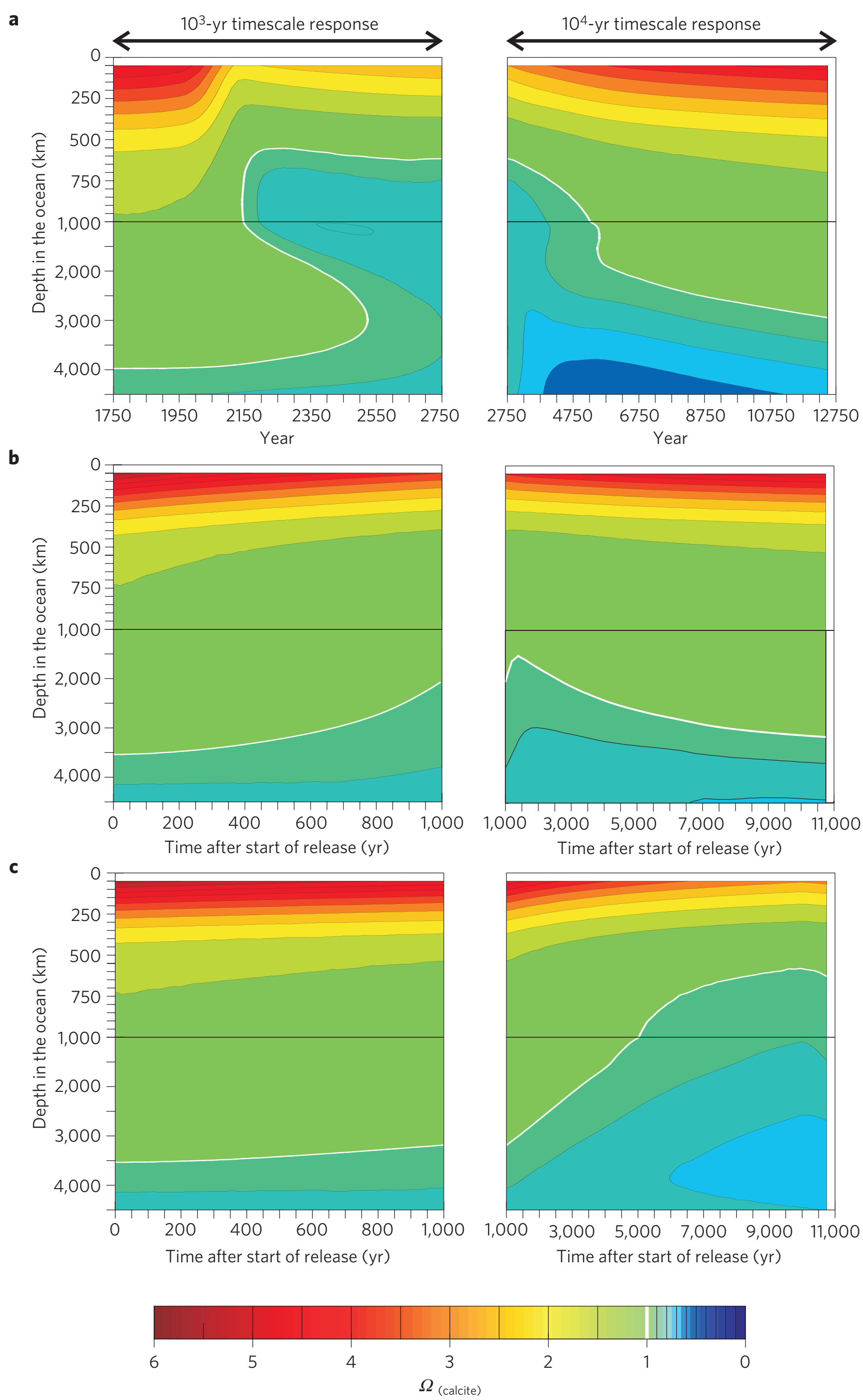

Figure 2 | Anthropogenic and PETM evolution of ocean carbonate saturation in the model. a, Time evolution of ocean $\Omega_{(calcite)}$ (horizontally averaged) under modern boundary conditions and in response to historical CO_2 emissions to 2000 then IS92a CO_2 emissions scenario[14] to 2100, with a linear decline to achieve a cumulative release of 2,180 PgC. **b**, Time evolution of ocean $\Omega_{(calcite)}$ (horizontally averaged) under late Palaeocene boundary conditions and in response to uniform 2,180 PgC release over 1 kyr. Despite starting slightly more undersaturated ($\Omega < 1.0$) than modern, the decrease in Ω at depth is less pronounced, partly a consequence of the higher calcium ion concentration of the Palaeocene ocean. **c**, Time evolution of ocean $\Omega_{(calcite)}$ (horizontally averaged) under late Palaeocene conditions and in response to uniform 6,840 PgC release over 10 kyr. All three experiments include both climate and deep-sea sedimentary feedbacks.

sufficiently long. The potential for 'flushing' of the deep ocean has important implications for the benthos, and occurs in addition to the collapse of the Atlantic meridional overturning circulation that acts to initially stagnate the deep North Atlantic Ocean.

There are a number of hypotheses for the extinction amongst microbenthos during the PETM, one of which is that the organism's oxygen demand could no longer be met, owing to a combination of higher metabolic rates (caused by higher temperature) and lower O_2 availability[7]. Any ventilation of the deep ocean that ameliorates bottom-water temperature and dissolved O_2 changes could thus help maintain tolerable benthic environmental conditions. However, if this process is coupled with severe undersaturation of the

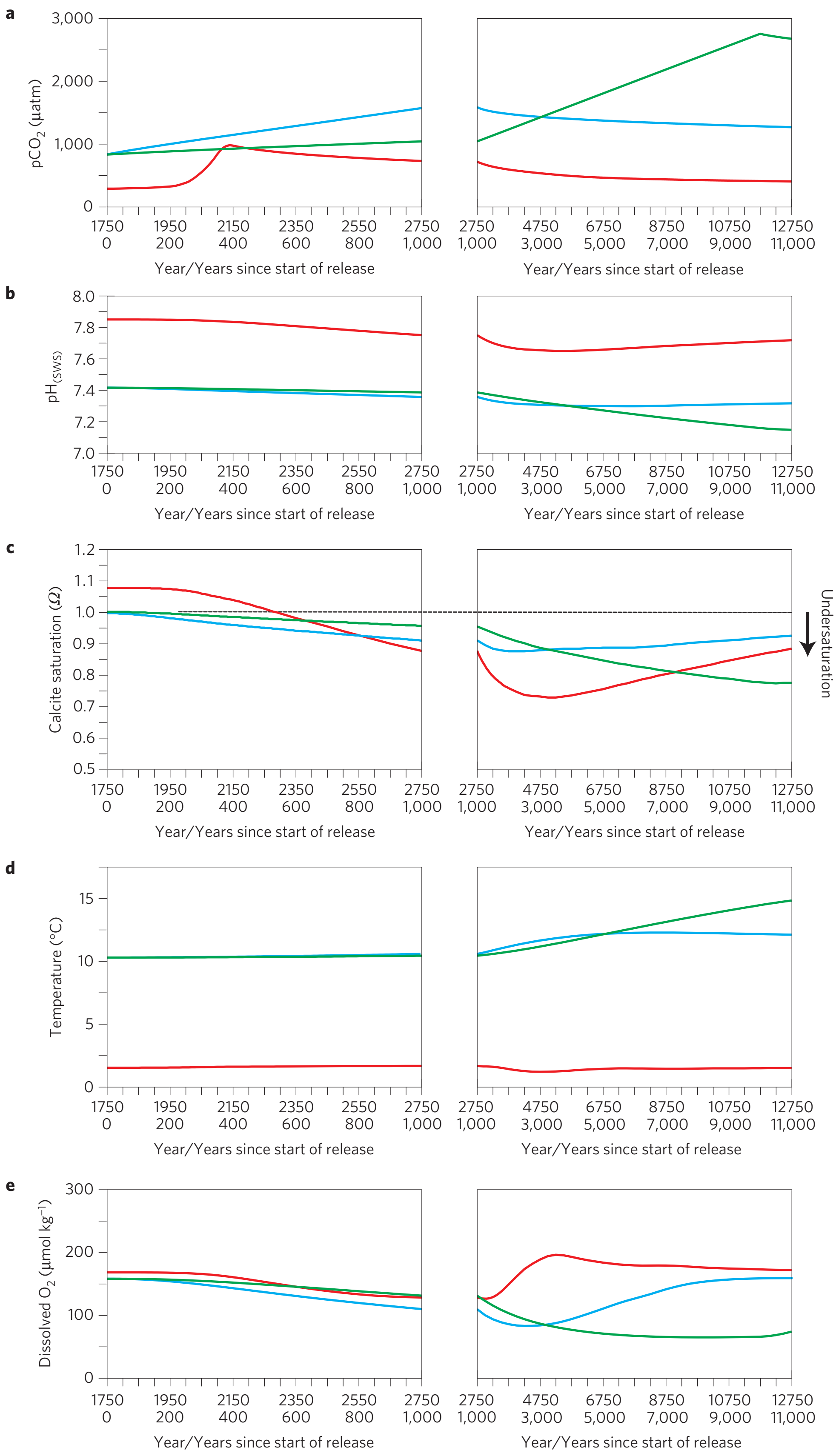

Figure 3 | Evolution of benthic environmental conditions in the model. a, For comparison, atmospheric CO_2. The red line reflects the modern Earth system response to IS92a (2,180 PgC total emissions as per Fig. 2a). The blue line reflects the Palaeogene Earth system response to 2,180 PgC release over 1 kyr and the green line 6,840 PgC over 10 kyr. **b–e**, Evolution of deep-sea conditions, as an area-weighted mean of seafloor conditions lying below 2 km water depth: $pH_{(SWS)}$ (**b**), calcite saturation (**c**), temperature (**d**) and dissolved oxygen concentration (**e**).

benthic environment (Fig. 3c), then benthic organisms may suffer stress owing to the severe carbonate chemistry changes. In this regard, it is notable that the extinction associated with the PETM was particularly strong amongst deep-sea calcifiers, whereas agglutinating, non-calcifying deep-sea species and shallow-water shelf taxa show significantly lower levels of extinction[7]. Ventilation events may be model dependent and millennial-scale future changes could be qualitatively different in the absence of significant changes in Atlantic meridional overturning. However, either endmember future consequence—poorly ventilated, warm and partly dysoxic[21,22] or ventilated but highly undersaturated—would represent a significant stressor on the benthos.

On the basis of our approach of paired Earth-system model simulations of past and future marine geochemical changes, we infer a future rate of surface-ocean acidification and environmental pressure on marine calcifiers unprecedented in the past 65 Myr, and one that challenges the potential for surface-ocean plankton to adapt. For benthic organisms, rapid and extreme undersaturation of the deep ocean would make their situation precarious, and the occurrence of widespread extinction of these organisms during the PETM greenhouse warming and acidification event raises the possibility of similar extinction in the future.

Methods

For future and PETM simulations, we use the Grid Enabled Integrated Earth system model (GENIE-1). GENIE-1 consists of a three-dimensional non-eddy-resolving frictional geostrophic ocean circulation model, two-dimensional sea ice and energy moisture balance atmospheric models and incorporates representations of the marine geochemical cycling of carbon and other biologically mediated tracers[23] plus preservation of carbonates in deep-sea sediments[24]. The modern configuration of GENIE-1, summarized in refs 16, 25, predicts year 1994 ocean anthropogenic CO_2 inventory and deep-ocean radiocarbon ages within observational error[25]. The PETM configuration is identical, apart from boundary conditions appropriate for the late Palaeocene: (1) 0.46% reduced solar constant (but modern orbit), (2) a continental configuration (Supplementary Fig. S1), annual average surface-ocean wind stress and wind speed, and zonally (and annually) averaged planetary albedo re-gridded from the coupled general circulation model of ref. 26 forced at $\times 3CO_2$, (3) 1‰ decrease in mean ocean salinity to account for the absence of significant land-based ice, (4) uniform $CaCO_3$/particulate organic carbon export ratio of 0.2 (ref. 13) and (5) an increase in the air–sea gas transfer coefficient (from 0.31 to 0.52) to re-scale (CO_2) gas transfer to the inferred modern value of $\sim$0.058 mol m^{-2} yr^{-1} µatm^{-1}. Initial late Palaeocene global carbon cycle conditions comprise: 834 ppm atmospheric CO_2, 18.22 mmol kg^{-1} Ca^{2+}, 29.89 mmol kg^{-1} Mg^{2+} and 15 mmol kg^{-1} SO_4^{2-}, following ref. 13. Alkalinity (1,975 µmol eq kg^{-1}) was chosen to produce a mean sediment $CaCO_3$ content (below 176 m water depth) of $\sim$50 wt% (Supplementary Fig. S1) and a global deep-sea sediment $CaCO_3$ burial rate of 15.4 Tmol Ca^{2+} yr^{-1} to closely match the optimal late Palaeocene sediment distribution determined by ref. 13. Ocean dissolved inorganic carbon is then constrained at 2,026 µmol kg^{-1}. We do not include the terrestrial biosphere in these simulations and thus our applied CO_2 emissions are the net of the uncertain response of the terrestrial carbon inventory. Once spun-up to steady state (100 kyr), all experiments are run for 110 kyr, of which we present only the first 11 kyr.

Received 29 September 2009; accepted 22 December 2009; published online 14 February 2010

References

1. Caldeira, K. & Wickett, M. E. Anthropogenic carbon and ocean pH. *Nature* **425,** 365–368 (2003).
2. Langer, G. *et al.* Species-specific responses of calcifying algae to changing seawater carbonate chemistry. *Geochem. Geophys. Geosyst.* **7,** Q09006 (2006).
3. Bijma, J., Spero, H. J. & Lea, D. W. in *Use of Proxies in Paleoceanography: Examples from the South Atlantic* (eds Fischer, G. & Wefer, G.) 489–512 (Springer, 1999).
4. Langdon, C. & Atkinson, M. J. Effect of elevated pCO_2 on photosynthesis and calcification of corals and interactions with seasonal change in temperature/irradiance and nutrient enrichment. *J. Geophys. Res.* **110,** C09S07 (2005).
5. Ridgwell, A. J. *et al.* From laboratory manipulations to Earth system models: Scaling calcification impacts of ocean acidification. *Biogeosciences* **6,** 2611–2623 (2009).
6. Kennett, J. P. & Stott, L. D. Abrupt deep-sea warming, paleoceanographic changes and benthic extinctions at the end of the Paleocene. *Nature* **353,** 225–229 (1991).
7. Thomas, E. in *Geological Society of America Special Paper* Vol. 424 (eds Monechi, S., Coccioni, R. & Rampino, M. R.) 1 (Geological Society of America, 2007).
8. Gibbs, S. J., Bown, P. R., Sessa, J. A., Bralower, T. J. & Wilson, P. A. Nannoplankton extinction and origination across the Paleocene–Eocene thermal maximum. *Science* **314,** 1770–1773 (2006).
9. Kelly, D. C., Bralower, T. J., Zachos, J. C., Silva, I. P. & Thomas, E. Rapid diversification of planktonic foraminifera in the tropical Pacific (ODP Site 865) during the late Paleocene thermal maximum. *Geology* **24,** 423–426 (1996).
10. Ridgwell, A. Changes in the mode of carbonate deposition: Implications for Phanerozoic ocean chemistry. *Mar. Geol.* **217,** 339–357 (2005).
11. Zachos, J. C. *et al.* Rapid acidification of the ocean during the Paleocene–Eocene thermal maximum. *Science* **308,** 1611–1615 (2005).
12. Goodwin, P., Williams, R. G., Ridgwell, A. & Follows, M. J. Climate sensitivity to the carbon cycle modulated by past and future changes in ocean chemistry. *Nature Geosci.* **2,** 145–150 (2009).
13. Panchuk, K., Ridgwell, A. & Kump, L. R. Sedimentary response to Paleocene Eocene thermal maximum carbon release: A model-data comparison. *Geology* **36,** 315–318 (2008).
14. Nakicenovic, N. & Stewart, R. (eds) *Emissions Scenarios: Special Report of the Intergovernmental Panel on Climate Change* (Cambridge Univ. Press, 2000).
15. Zeebe, R. E., Zachos, J. C. & Dickens, G. R. Carbon dioxide forcing alone insufficient to explain Palaeocene–Eocene thermal maximum warming. *Nature Geosci.* **2,** 576–580 (2009).
16. Archer, D. *et al.* Atmospheric lifetime of fossil-fuel carbon dioxide. *Annu. Rev. Earth Planet. Sci.* **37,** 117–134 (2009).
17. Davis, M. B., Shaw, R. G. & Etterson, J. R. Evolutionary responses to changing climate. *Ecology* **86,** 1704–1714 (2005).
18. Santiago, F. E. & Sanjuan, R. Climb every mountain? *Science* **302,** 2074–2075 (2003).
19. Buckling, A., Wills, M. A. & Colegrave, N. Adaptation limits diversification of experimental bacterial populations. *Science* **302,** 2107–2109 (2003).
20. Meissner, K. J., Eby, M., Weaver, A. J. & Saenko, O. A. CO_2 threshold for millennial-scale oscillations in the climate system: Implications for global warming scenarios. *Clim. Dyn.* **30,** 161–174 (2008).
21. Shaffer, G., Olsen, S. M. & Pedersen, J. O. P. Long-term ocean oxygen depletion in response to carbon dioxide emissions from fossil fuels. *Nature Geosci.* **2,** 105–109 (2009).
22. Hofmann, M. & Schellnhuber, H.-J. Oceanic acidification affects marine carbon pump and triggers extended marine oxygen holes. *Proc. Natl Acad. Sci. USA* **106,** 3017–3022 (2009).
23. Ridgwell, A. *et al.* Marine geochemical data assimilation in an efficient Earth system model of global biogeochemical cycling. *Biogeosciences* **4,** 87–104 (2007).
24. Ridgwell, A. J. & Hargreaves, J. C. Regulation of atmospheric CO_2 by deep-sea sediments in an Earth system model. *Glob. Biogeochem. Cycles* **21,** GB2008 (2007).
25. Cao, L. *et al.* The role of ocean transport in the uptake of anthropogenic CO_2. *Biogeosciences* **6,** 375–390 (2009).
26. Tindall, J. C. *et al.* Modeling the oxygen isotope distribution of ancient seawater using a coupled ocean-atmosphere GCM: Implications for reconstructing early Eocene climate. *Earth Planet. Sci. Lett.* (in the press).
27. Martin, R. E. Cyclic and secular variation in microfossil biomineralization—clues to the biogeochemical evolution of Phanerozoic oceans. *Glob. Planet. Change* **11,** 1–23 (1995).
28. Tyrrell, T. & Zeebe, R. E. History of carbonate ion concentration over the last 100 million years. *Geochim. Cosmochim. Acta* **68,** 3521–3530 (2004).

Acknowledgements

A.R. and D.N.S. acknowledge support from The Royal Society in the form of University Research Fellowships, the UK National Environmental Council grants NE/F001622/1 and NE/F002408/1, together with NSF EAR-0628719. This work arose out of the IGBP-SCOR Fast Track Initiative on Ocean Acidification and is a contribution to the EU EPOCA ocean acidification initiative.

Author contributions

A.R. conceived and analysed the model experiments. Both authors discussed the results and wrote the paper.

Additional information

The authors declare no competing financial interests. Supplementary information accompanies this paper on www.nature.com/naturegeoscience. Reprints and permissions information is available online at http://npg.nature.com/reprintsandpermissions. Correspondence and requests for materials should be addressed to A.R.