



Rapid ocean acidification and protracted Earth system recovery followed the end-Cretaceous Chicxulub impact

Michael J. Henehan^{a,b,1}, Andy Ridgwell^{c,d}, Ellen Thomas^{a,e}, Shuang Zhang^a, Laia Alegret^f, Daniela N. Schmidt^g, James W. B. Rae^h, James D. Witts^{i,j}, Neil H. Landmanⁱ, Sarah E. Greene^k, Brian T. Huber^l, James R. Super^a, Noah J. Planavsky^a, and Pincelli M. Hull^{a,1}

^aDepartment of Geology & Geophysics, Yale University, New Haven, CT 06520; ^bSection 3.3, Deutsches GeoForschungsZentrum GFZ, 14473 Potsdam, Germany; ^cSchool of Geographical Sciences, Bristol University, Bristol BS8 1SS, United Kingdom; ^dDepartment of Earth Sciences, University of California, Riverside, CA 92521; ^eDepartment of Earth and Environmental Sciences, Wesleyan University, Middletown, CT 06459; ^fInstituto Universitario de Investigación en Ciencias Ambientales de Aragón, Departamento de Ciencias de la Tierra, Universidad de Zaragoza, 50009 Zaragoza, Spain; ^gSchool of Earth Sciences, University of Bristol, Bristol BS8 1RJ, United Kingdom; ^hSchool of Earth & Environmental Sciences, University of St. Andrews, St. Andrews KY16 9AL, United Kingdom; ⁱDivision of Paleontology, American Museum of Natural History, New York, NY 10024; ^jDepartment of Earth and Planetary Sciences, University of New Mexico, Albuquerque, NM 87131; ^kSchool of Geography, Earth and Environmental Sciences, University of Birmingham, Birmingham B15 2TT, United Kingdom; and ^lDepartment of Paleobiology, Smithsonian Institution, Washington, DC 20560

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Mass extinction at the Cretaceous–Paleogene (K–Pg) boundary coincides with the Chicxulub bolide impact and also falls within the broader time frame of Deccan trap emplacement. Critically, though, empirical evidence as to how either of these factors could have driven observed extinction patterns and carbon cycle perturbations is still lacking. Here, using boron isotopes in foraminifera, we document a geologically rapid surface-ocean pH drop following the Chicxulub impact, supporting impact-induced ocean acidification as a mechanism for ecological collapse in the marine realm. Subsequently, surface water pH rebounded sharply with the extinction of marine calcifiers and the associated imbalance in the global carbon cycle. Our reconstructed water-column pH gradients, combined with Earth system modeling, indicate that a partial ~50% reduction in global marine primary productivity is sufficient to explain observed marine carbon isotope patterns at the K–Pg, due to the underlying action of the solubility pump. While primary productivity recovered within a few tens of thousands of years, inefficiency in carbon export to the deep sea lasted much longer. This phased recovery scenario reconciles competing hypotheses previously put forward to explain the K–Pg carbon isotope records, and explains both spatially variable patterns of change in marine productivity across the event and a lack of extinction at the deep sea floor. In sum, we provide insights into the drivers of the last mass extinction, the recovery of marine carbon cycling in a postextinction world, and the way in which marine life imprints its isotopic signal onto the geological record.

Here we apply the boron isotope-pH proxy to planktic and benthic foraminifera to examine whether ocean acidification occurred at the K–Pg boundary and to test competing hypotheses that have been proposed to explain changes in the marine carbon cycle in the aftermath of the mass extinction. We analyzed material from multiple sites where sufficient well-preserved foraminifera from the mixed layer of the surface ocean could be obtained, with >7,000 small, thin-walled postextinction foraminifera required per analysis in some cases. By combining measurements from continental shelf sites in communication with the open ocean [Geulhemmerberg Cave, The Netherlands (6), Owl Creek, Mississippi (7), and Brazos River, Texas (8)] and deep-sea drilling sites (Deep-Sea Drilling Program Site 465 and Ocean Drilling Program [ODP] Site 1209 in the Pacific and ODP Site 1049 in the Atlantic), we construct a composite global record spanning ~800 ky (*SI Appendix*). Importantly, one shallow marine sample site studied

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Significance

Debate lingers over what caused the last mass extinction 66 million years ago, with intense volcanism and extraterrestrial impact the most widely supported hypotheses. However, without empirical evidence for either's exact environmental effects, it is difficult to discern which was most important in driving extinction. It is also unclear why recovery of biodiversity and carbon cycling in the oceans was so slow after an apparently sudden extinction event. In this paper, we show (using boron isotopes and Earth system modeling) that the impact caused rapid ocean acidification, and that the resulting ecological collapse in the oceans had long-lasting effects for global carbon cycling and climate. Our data suggest that impact, not volcanism, was key in driving end-Cretaceous mass extinction.

There is abundant evidence for a massive bolide impact at the Cretaceous–Paleogene (K–Pg) boundary (66.04 Ma) that coincides in those sections with sufficient temporal resolution with a mass extinction horizon (e.g., ref. 1). Geological records document many effects from impact, including massive tsunamis, earthquake-driven gravity flows, and molten ejecta fallout (e.g., ref. 1). However, the mechanism (or mechanisms) by which impact drove global-scale ecosystem turnover and mass extinction is less certain. Among the most prominent hypotheses are global darkness and associated primary productivity loss leading to food chain collapse, acid rain, impact winter, and flash ocean acidification (2). Some of these mechanisms are supported by modeling work (e.g., ref. 3) but, critically, they generally lack empirical validation. Furthermore, the issue is complicated by the possibility of contributing effects from ongoing or intensified Deccan flood basalt volcanism (4, 5) and the short timescales of at least some of the effects of impact compared to the resolution of the geological record.

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The authors declare no competing interest.

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¹To whom correspondence may be addressed. Email: michael.henehan@gfz-potsdam.edu or pincelli.hull@yale.edu.

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here (Geulhemmerberg Cave) is thought to preserve sediments from the first 10^2 to 10^3 y after bolide impact (6), allowing us to pinpoint a short-lived signal of impact-induced ocean acidification that cannot be temporally resolved in deep marine records. Samples from ODP Site 1209 allow us to investigate longer-term changes in the ocean's biological carbon pump as expressed in vertical pH gradients, as this site is one of few deep marine K-Pg boundary sites that preserves sufficient numbers of well-preserved epifaunal benthic and surface-dwelling planktic foraminifera for boron isotope analysis. The broad range of in situ temperatures, hydrostatic pressures, and environmental conditions represented in our sample set allows us to constrain bulk seawater $\delta^{11}\text{B}$ ($\delta^{11}\text{B}_{\text{sw}}$; see *SI Appendix*), one of the main uncertainties in calculating pH from deep-time $\delta^{11}\text{B}$ measurements. Assuming feasible limits on the calcium carbonate saturation state (Ω_{CaCO_3}) and oxygen utilization at each site (see *SI Appendix, section 5C*), we constrain K-Pg $\delta^{11}\text{B}_{\text{sw}}$ to within 39.05 to 39.85‰.

Our data suggest ocean pH was stable over the last 100 ky of the Cretaceous, despite suggestions of a major pulse of Deccan volcanism within this time interval (5). However, our data from the Geulhemmerberg Cave boundary clay indicate a marked ~ 0.25 pH unit surface ocean acidification event within a thousand years (6) of the bolide impact in the Geulhemmerberg Cave boundary clay (Fig. 1C). These data provide geochemical evidence of rapid acidification in the immediate aftermath of the Chicxulub impact.

Combined with model-derived estimates of alkalinity (*SI Appendix*), this change in pH corresponds to a rise in atmospheric partial pressure of CO_2 ($p\text{CO}_2$) from ~ 900 ppm in the latest Maastrichtian to $\sim 1,600$ ppm in the immediate aftermath of bolide impact (Fig. 1D). This measured pH drop may be a conservative estimate of the full magnitude of impact-induced acidification, as the earliest Ir-rich ejecta layer at Geulhemmerberg is thought to have been eroded within ~ 100 y of the impact (6). A geologically rapid 0.2 to 0.3 pH unit change would have disadvantaged calcifying plankton vs. noncalcifiers (9) and could therefore explain the selective extinction of calcifying pelagic organisms during the K-Pg mass extinction (10–13) compared to noncalcareous groups such as dinoflagellates (e.g., ref. 14) and radiolarians (e.g., ref. 15). Similarly, since coccolithophores and planktic foraminifera from coastal areas may be better adapted to fluctuations in pH (16), and smaller foraminifera may better maintain calcification under low pH (17), acidification could also help to explain on-shelf/off-shelf and size-selective patterns of extinction among calcifiers (18, 19). The observed magnitude of acidification is compatible with the rainout of SO_2 and NO_x released by the impactor (10, 20, 21), depending on the timing of sediment deposition at Geulhemmerberg. The effect of rainout products was transient (e.g., ref. 21), and if Geulhemmerberg clays were deposited on timescales greater than a few hundred years, a contribution to acidification from CO_2 release would have been required. This additional CO_2

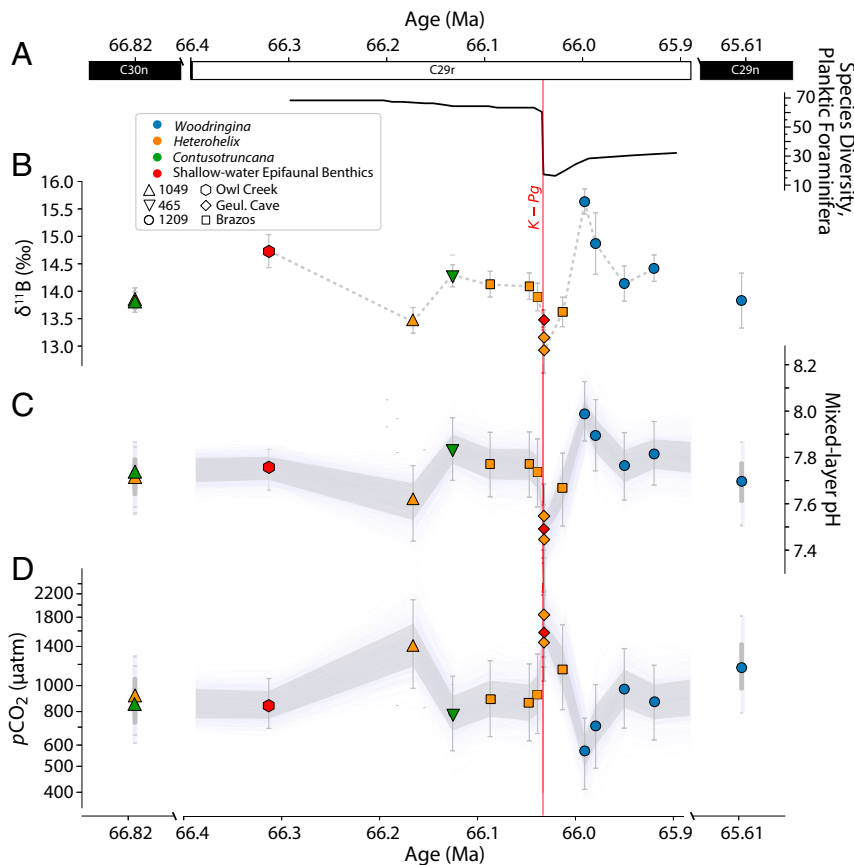


Fig. 1. Records of surface ocean foraminiferal $\delta^{11}\text{B}$ (B), calculated pH (C), and $p\text{CO}_2$ (D) across the K-Pg boundary, with high-resolution foraminiferal diversity counts from ref. 39 at the K-Pg Global Boundary Stratotype Section and Point (El Kef) plotted for context (A). pH is calculated assuming our best estimate of K-Pg $\delta^{11}\text{B}_{\text{sw}}$ $39.45 \pm 0.4\text{‰}$. $p\text{CO}_2$ is calculated from pH along with total alkalinity estimates at each site from a GENIE late Maastrichtian simulation, adjusted for dynamic changes in alkalinity across the K-Pg using LOSCAR simulations from ref. 22 that match observed patterns of carbonate burial. Gray shaded areas are 1-sigma uncertainties, with thin lines representing 1,000 Monte Carlo simulations from the 10,000 that were run. For clarity, we only plot those samples that represent the surface mixed layer, which should be approximately in equilibrium with the atmosphere. Additional data from deep-sea benthic and thermocline-dwelling planktic foraminifera that do not reflect atmospheric $p\text{CO}_2$ can be seen in Fig. 2 and in *Dataset S1*. For details of the age models used, the estimation of $\delta^{11}\text{B}_{\text{sw}}$ carbonate system calculations, and uncertainty propagation see *SI Appendix*.

could be sourced from carbonate target rocks (ref. 1 and references therein), the biosphere [through wildfires and decay (ref. 1 and references therein)], a transient weakening of the biological carbon pump (ref. 22 and references therein and *SI Appendix*), and/or a contribution from a pulse of volcanism (5).

Loss of plankton functional groups with the K-Pg impact has profound implications for marine carbon cycling (22), manifest in one of the earliest and most striking geochemical observations of the K-Pg boundary in open ocean sediments: a convergence in the $\delta^{13}\text{C}$ values of surface- and deep-dwelling calcifiers (e.g., ref. 23). Paired measurements of $\delta^{11}\text{B}$ (and hence pH) from surface and deep water after the K-Pg boundary allow us to address a long-running, unresolved debate about the cause of this convergence, and the long-term effect of the K-Pg mass extinction on marine carbon cycling. Surface ocean $\delta^{13}\text{C}$ is typically maintained at heavy values relative to the deep sea through the biological pump, which exports isotopically light organic carbon from the surface ocean to depth. The sharp drop in surface ocean $\delta^{13}\text{C}$ at the K-Pg was therefore initially interpreted as a near-total loss of marine new primary productivity after impact, in the “Strangelove Ocean” hypothesis (24). Later, the “Living Ocean” hypothesis (25) posited that such a reduction of vertical $\delta^{13}\text{C}$ gradients arose instead from a decrease in the efficiency of the biological pump, that is, continued productivity but reduced sinking efficiency leading to more remineralization of organic carbon in the upper water column. Evidence for export to the deep ocean persisting in at least some regions led to the “Heterogeneous Ocean” hypothesis (11, 26), while it has also been argued that part of the reduction in $\delta^{13}\text{C}$ gradients stems from the fact that carbon isotope vital effects differ in postextinction carbonate producers compared to the pre-extinction ones (11, 27). These latter scenarios appear more compatible with low levels of benthic foraminiferal extinction at the K-Pg (11, 28) than a near-total loss of primary or export production. Another alternative hypothesis not linked to any marine biogeochemical response is that extremely high atmospheric $p\text{CO}_2$ (thousands of parts per million) could have driven convergence in deep- and surface-ocean $\delta^{13}\text{C}$ inorganically (29). Such a

scenario might arise if outgassing from the Deccan Traps was accelerated following the impact (4).

Our records show that initial surface acidification was followed by a rapid rebound and overshoot in surface ocean pH ($\Delta\text{pH} \approx 0.5$) within 40 ky of the K-Pg boundary, returning to preevent values after an additional ~ 80 ky (Fig. 1A). This is consistent with model predictions of ocean pH rise due to the extinction of calcifying organisms and a consequent transient reduction in the marine alkalinity sink (22, 30). Such a period of imbalance in marine alkalinity fluxes in the earliest Danian is supported by observations of improved deep-sea carbonate preservation (22), the occurrence of heavily calcified deep-sea benthic foraminifera (31), and the deposition of abiogenic calcite crystals in the oceans (32). The absence of any prolonged (>50 ky) surface ocean acidification after the K-Pg suggests, therefore, that if there were a state shift toward significantly more active Deccan CO_2 degassing in response to impact (4), its effects were overwhelmed by the biogeochemical effect of extinction. Other independent $p\text{CO}_2$ proxy records (e.g., ref. 33) likewise do not support a substantial rise in CO_2 , and there is no evidence for deep-sea warming at this time (34). Thus, we discount high $p\text{CO}_2$ as the driver of reduced vertical $\delta^{13}\text{C}$ gradients (29) and infer that the convergence in surface and deep-ocean $\delta^{13}\text{C}$ arose from a change in oceanic biogeochemical cycling, combined to some extent with changes in carbonate vital effects.

To explore how changes in the carbon cycle would manifest in vertical pH and $\delta^{13}\text{C}$ gradients, we used GENIE (Grid ENabled Integrated Earth System Model) (35), with a late Maastrichtian bathymetry and continental configuration (*SI Appendix*, Fig. S17 and *SI Appendix*). We simulate the response of marine $\delta^{13}\text{C}$ and pH given either reduced or zero primary productivity (a “Strangelove Ocean”-type scenario) or less efficient biological pump (i.e., enhanced remineralization in the upper water column, “Living Ocean” scenario; full details are given in *SI Appendix*). For each simulation, we show depth transects for $\delta^{13}\text{C}$ and pH at Shatsky Rise (ODP Site 1209) (Fig. 2 B and C). Pacific basin $\delta^{13}\text{C}$ zonal means for 3 illustrative states of biological pumping are shown in

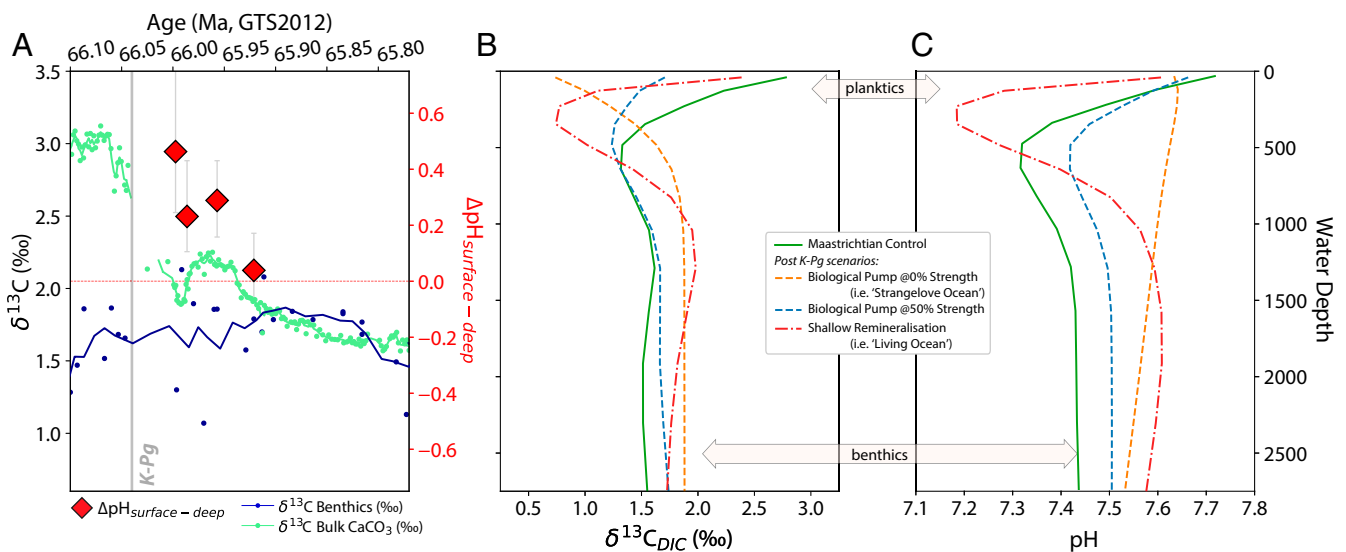


Fig. 2. Paired benthic-planktic foraminiferal $\delta^{11}\text{B}$ measurements from 4 time slices following the K-Pg boundary at ODP Site 1209 (Shatsky Rise) are used to calculate the difference in surface and deep ocean pH (ΔpH ; red diamonds, A). These data show a trend from “normal” patterns of higher $\delta^{11}\text{B}/\text{pH}$ in the surface ocean relative to the deep until 65.92 Ma, where this gradient disappears (see also *SI Appendix*, Fig. S12). Shown for context is the convergence in $\delta^{13}\text{C}$ from surface waters (bulk CaCO_3 , in green) and deep ocean waters (benthic foraminifera, navy) (A). Water column $\delta^{13}\text{C}$ and pH profiles in the cGENIE model the location of Shatsky Rise (see also Fig. 3) are shown in B and C, respectively. A weakened or reversed $\delta^{13}\text{C}$ gradient can arise in a number of ways (B), but only a shallow remineralization (or “Living Ocean,” red dot-dashed line) model can produce a flat gradient in pH between the surface 80 m and 2,500-m water depth (C). Carbonate data from ODP 1209 include new data and benthic data from ref. 34. See *SI Appendix* for more details.

shows that even geologically rapid ocean acidification events can have prolonged and profound biotic ramifications.

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