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

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Mass extinction at the Cretaceous–Paleogene (K-Pg) boundary coincides with the Chixculub 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 Chixculub 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 phase recovered 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.

Cretaceous/Paleogene boundary | ocean acidification | boron isotopes | mass extinction | GENIE model

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.

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

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.

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here (Geulhemmerberg Cave) is thought to preserve sediments from the first 10° to 10^4 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 δ^{11}B (δ^{11}B_{sw}; see SI Appendix), one of the main uncertainties in calculating pH from deep-time δ^{11}B measurements. Assuming feasible limits on the calcium carbonate saturation state (Ω_{CaCO3}) and oxygen utilization at each site (see SI Appendix, section 5C), we constrain K-Pg δ^{11}B_{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 (pCO_2) from ~900 ppm in the latest Maastrichtian to ~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. noncalcarious (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_3 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

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**Fig. 1.** Records of surface ocean foraminiferal δ^{11}B (B), calculated pH (C), and pCO_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 δ^{11}B_{sw}, 39.45 ± 0.04‰. pCO_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 pCO_2 can be seen in Fig. 2 and in Dataset S1. For details of the age models used, the estimation of δ^{13}C_{sw} carbonate system calculations, and uncertainty propagation see SI Appendix.
Paired benthic red dot-dashed line) model can produce a flat gradient in pH between the surface and 2,500-m water depth (www.pnas.org/cgi/doi/10.1073/pnas.1905989116). Patterns of higher pH at the K-Pg (11, 26) than a near-total loss of primary or export remineralizaton 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 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 CO2 degassing in response to impact (4), its effects were overwhelmed by the biogeochemical effect of extinction. Other independent pCO2 proxy records (e.g., ref. 33) likewise do not support a substantial rise in CO2 and there is no evidence for deep-sea warming at this time (34). Thus, we discount high pCO2 as the driver of reduced vertical δ13C gradients (29) and infer that the convergence in surface and deep-ocean δ13C 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 δ13C 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 δ13C 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 δ13C and pH at Shatsky Rise (ODP Site 1209) (Fig. 2 B and C). Pacific basin δ13C zonal means for 3 illustrative states of biological pumping are shown in Supplementary Figure S12.

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**Fig. 2.** Paired benthic–planktic foraminiferal δ18O 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 δ18O/δ13C 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 δ13C from surface waters (bulk CaCO3 in green) and deep ocean waters (benthic foraminifera, navy) (A). Water column δ13C and pH profiles in the GENIE model the location of Shatsky Rise (see also Fig. 3) are shown in B and C, respectively. A weakened or reversed δ13C 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.

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A scenario with a complete loss of productivity is a lighter than benthic (Fig. 2 and 3 at colder, higher latitudes is driven higher with respect to δ\(^{13}\)C, with most positive values at the surface (Fig. 3A and SI Appendix). Somewhere between a “Strangelove”-style shutdown and a full-strength biological pump, there must exist a weaker state of the biological pump that would impart a δ\(^{13}\)C gradient opposite in sign and equal in magnitude to the solubility pump, canceling out the difference in δ\(^{13}\)C between surface and deep ocean. We find this occurs with a 50% reduction in global export production for all but the highest-latitude Northern Pacific, where downwelling waters overlay an older (and lower δ\(^{13}\)C) lens of southern-sourced water (Figs. 2B and 3B). This partially maintained productivity is consistent with the survival of benthic foraminifera at the K-Pg (11, 28).

The combination of our CGENIE simulations and the observed sequence of changes in vertical pH and δ\(^{13}\)C gradients at Shatsky Rise (Fig. 2A) allow us to propose a hypothesis for the behavior of the marine carbon cycle after the K-Pg impact. During the first tens of thousands of years following impact, reduced vertical δ\(^{13}\)C gradients without an associated collapse in pH gradients (Fig. 2A) are consistent with a substantial reduction in new primary productivity globally following mass extinction (Fig. 2 B and C and SI Appendix). The magnitude of productivity loss required depends on changes in carbon isotope vital effects in pelagic CaCO\(_3\) producers, which likely account for some (but not all) of the observed collapse in δ\(^{13}\)C gradients (11, 27, 36). Reduced global export productivity can, however, align with published observations of a “Heterogeneous Ocean” with stable or increased productivity at certain sites (e.g., Shatsky Rise (11, 26)). A global reduction in new primary productivity may have led to a build up of nutrients in the surface ocean, and thus some locations (e.g., highly oligotrophic gyres) may have supported increased new/export primary productivity in the Danian relative to their preimpact state, even while export productivity globally was reduced (SI Appendix, Figs. S23 and S24).

After this period of globally reduced, but not collapsed, export productivity, we see a convergence in shallow and deep-ocean pH in our final time-slice ~120 ky post-K-Pg (Fig. 2A). In our model scenarios, only by remineralizing organic carbon shallower in the water column can one produce similar pH gradients between the surface sea and the subsurface (Fig. 2C). Shallow water remineralization alone (i.e., a “Living Ocean” scenario) does not fully collapse the δ\(^{13}\)C gradient in our model, but combined with known carbon-isotope vital effects that drive surface-derived carbonates lighter than ambient δ\(^{13}\)C\(_{DIC}\) (27, 36, 37) the expression of such a scenario in the fossil record could be a full collapse. We therefore suggest that after an initial period (up to 40 ky) of globally partially weakened new primary productivity globally, it progressively began to recover, but without full restoration of pelagic ecosystem structure and function. In such a scenario, persistently ineffective ballasting of marine organic matter or other factors could have then resulted in more organic material being remineralized shallower in the water column [i.e., a “Living Ocean” scenario (25)], thereby reducing δ\(^{13}\)C and pH gradients between the surface and deep sea.

Reduced vertical δ\(^{13}\)C\(_{CaCO3}\) gradients persisted for over 1 My after the K-Pg impact (e.g., ref. 27), which suggests that the efficiency of organic carbon export to the deep sea, a key pelagic ecosystem function, was reestablished slowly. Our δ\(^{15}\)N data do not support prolonged surface ocean acidification, making it difficult to attribute this delayed biogeochemical recovery to acidification from sustained (or enhanced) CO\(_2\) degassing from the Deccan Traps. Rather, there may be intrinsic constraints on the time required to recover normal marine ecosystem function after such severe global perturbations, despite the short generation times that should make marine plankton ideally suited to rapid evolutionary radiation (38). In this way, the K-Pg event...
shows that even geologically rapid ocean acidification events can have prolonged and profound biotic ramifications.

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