

# Paleo-ocean acidification and carbon cycle perturbation events

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Ocean acidification is a current area of concern for the future functioning of marine ecosystems and ocean biogeochemical cycles. The term “ocean acidification” describes the effects of the oceanic uptake of anthropogenic CO<sub>2</sub> including a progressive decrease of seawater-pH. While seawater is not likely to ever become acidic, a reduction in pH and associated carbonate system changes may nevertheless affect ocean biogeochemical processes, particularly biological calcification. However, modern ocean observations and laboratory experiments consider time scales that are too short to reveal the long-term potential of marine organisms to acclimatize or adapt to changing environmental conditions. Furthermore, as experiments focus on a few species or isolated strains, they provide little information on the potential for whole ecosystem changes. The U.S. National Science Foundation (NSF) and PAGES jointly sponsored this workshop to bring together an international group of carbon cycle modelers, carbonate chemistry specialists, and biological, chemical and physical (paleo-) oceanographers to discuss past carbon cycle perturbations and the long-term response of marine organisms to changing conditions, and to provide a geological perspective on future concerns.

Richard Zeebe (University of Hawaii) and Andy Ridgwell (University of Bristol) presented the boundary conditions of past marine carbonate chemistry and stressed the importance of distinguishing between extended periods of high pCO<sub>2</sub> with relatively slowly evolving ocean carbonate chemistry, and geologically rapid changes which reflect chemical effects more comparable to the consequence of ongoing CO<sub>2</sub> emissions. Acknowledging that the rate of anthropogenic CO<sub>2</sub> emissions is probably unparalleled in recent Earth history, Zeebe defined an “ocean acidification event” as one having a duration shorter than about 10 ka. Pleistocene glacial to interglacial transitions and early Cenozoic hyperthermals fall under this definition, but the only event that may be comparable in magnitude of CO<sub>2</sub> release is the Paleocene-Eocene Thermal Maximum (PETM).

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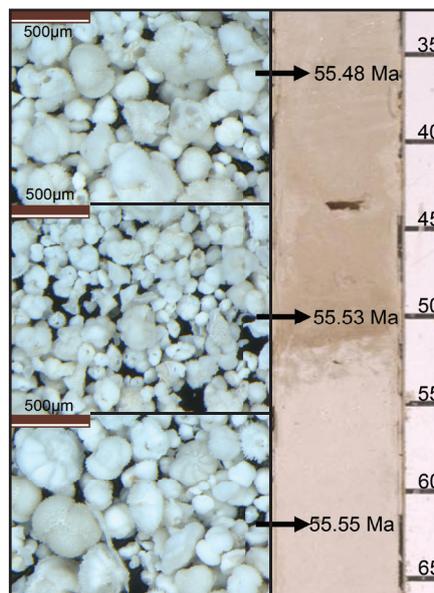


Figure 1: Core section from Shatsky Rise ODP Site 1210A, showing reduced carbonate preservation at the Paleocene-Eocene Thermal Maximum. During the PETM 30-50% of deep-sea benthic foraminifer species suffered extinction (Thomas, 1998). The scale bar on the right indicates depth of the core section in cm, which reflects on the lower sedimentation rate after the onset of the event. Picture credit: Laura Foster, University of Bristol; dates after Westerhold et al. (2008).

Southampton) reiterated the importance of the rate of environmental change in assessing the potential for future changes in marine ecosystems. They also focused on the complications associated with attributing biological responses to paleo-ocean acidification. Identifying stressful conditions at the sea surface, which would affect organisms' biology including calcification, is often indistinguishable from competing factors affecting preservation at the seafloor. Similarly, synergistic effects of temperature or nutrient changes cannot necessarily be separated from shifts in ocean carbonate chemistry. Independent proxy evidence is therefore of utmost importance to identify the physical and chemical boundary conditions that led to physiological and ecological shifts. In addition, the fossil record is biased towards those organisms that secrete skeletal hard parts, in particular marine calcifiers. Ecologically important phyto- and zooplankton are rarely preserved in the sediment and little is known about their fate under past ocean acidification conditions.

Proxies for ocean carbonate chemistry include the boron isotope proxy for seawater-

ter-pH, the carbon isotopic composition of alkenones for aqueous [CO<sub>2</sub>], foraminiferal B/Ca and U/Ca ratios for bottom-water carbonate saturation and carbonate ion concentration, foraminiferal shell weights, and the depth of the carbonate compensation depth to constrain whole-ocean carbonate saturation. Gavin Foster (NOC Southampton) and Jimin Yu (LDEO) presented proxy comparisons and recent advances in paleo-pH reconstructions. They demonstrated that quantitative reconstructions beyond the Pleistocene glacial/interglacial cycles are limited by uncertainties on the elemental and isotopic composition of seawater, and the lack of estimates on a second parameter of the carbon system from the same surface or deep-ocean environment. In addition, most of the established proxies are based on marine carbonates. This is problematic for ocean acidification events in which widespread dissolution of carbonates occurs, such as during the peak of the PETM (when only clays and organic molecules were preserved in many Atlantic sediments) (e.g., Fig. 1). As a novel approach to address this issue, Appy Sluijs (University of Utrecht) presented promising findings on the carbon isotopic composition of organic dinoflagellate cysts as a candidate proxy for aqueous CO<sub>2</sub>.

The workshop reiterated that no perfect analogue to anthropogenic ocean acidification has yet been found in Earth's geological record, but that an improved knowledge of the physicochemical boundary conditions in the surface and deep ocean, their rates and magnitudes and biological responses will nevertheless place important constraints on the consequences of current and future ocean acidification. A more comprehensive report on the rates, magnitudes and evidence for paleo-ocean acidification will be published as a peer-reviewed paper.

## References

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