

Comment on “Calcareous Nannoplankton Response to Surface-Water Acidification Around Oceanic Anoxic Event 1a”

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Erba *et al.* (Reports, 23 July 2010, p. 428) attributed calcareous nannofossil morphology and assemblage changes across Cretaceous Oceanic Anoxic Event 1a to the effects of surface ocean acidification. We argue that the quality of carbonate preservation in these sequences, the unsupported assumptions of the biotic response to acidity, and the absence of independent proxy estimates for ocean pH or atmospheric $p\text{CO}_2$ render this conclusion questionable.

The current increase in atmospheric CO_2 ($p\text{CO}_2$) is causing a decrease in surface-ocean pH (1). Laboratory and field experiments on calcifying organisms indicate a range of responses to acidification, including both disrupted and increased calcification (2, 3). Geological records complement modern observational data by providing records on longer time scales (10^2 to 10^6 years), integrating short-term physiological and longer-term evolutionary responses to elevated $p\text{CO}_2$. However, to demonstrate a link between fossil records and paleo-ocean acidification requires robust and independent estimates of ocean pH and carbonate chemistry and consideration of accompanying environmental changes.

Perturbations documented in the plankton and carbonate platform fossil records of Mesozoic oceanic anoxic events (OAEs) are increasingly attributed to ocean acidification in an emerging paradigm of ancient biocalcification crises (4). In this vein, Erba *et al.* (5) attribute changes in calcareous nannoplankton before and during Oceanic Anoxic Event 1a (OAE1a) to the effects of surface ocean acidification. Our concerns with their conclusions are threefold.

First, multiple environmental and preservation factors influence the composition of nannofossil assemblages and must be given due consideration before concluding a surface ocean acidification effect. Erba *et al.* used “paleoflux” for the accumulation rates of their total nannofossil assemblage and imply that these correspond to primary plankton production controlled

predominantly by $p\text{CO}_2$. Accumulation rates are, however, the end result of the complex interplay between surface water productivity, dissolution during transport and burial, sediment dilution, and diagenesis. The link to $p\text{CO}_2$ is based on extrapolation from calcification changes reported in culture experiments (4), but the assumption that such change within a modern species or strain is an identical process to assemblage-wide carbonate production is questionable. In addition, dissolution is clearly a major control here, because these assemblages have less than half the diversity of global estimates of this age (6). Also, the effects of warming and eutrophication are widely cited as factors controlling plankton evolution and assemblages at OAE1a (7, 8).

Furthermore, the assumption that coccolith size change per se is an indication of acidification is unsupported. Coccolith size tracks cell size (9), and there is no reason to predict that ocean acidification would result in either an increase or decrease in cell size. Rather, a change in the degree of calcification of the same-sized coccoliths would be a better indicator of a carbonate chemistry response. Finally, the abundance decline in nannoconids (the “nannoconid crisis”) is solely attributed to the effects of surface ocean acidification, based on the assumption that heavily calcified taxa would be more susceptible than weakly calcified forms. However, the most substantial reduction in their abundance occurred 1 million years before the OAE1a, where there is no correlation to any geochemical ($\delta^{18}\text{O}$ or $\delta^{13}\text{C}$) or lithological change.

Overall, it is circular to identify acidification and CO_2 pulses by plankton response and then to use this evidence to prove that calcifying plankton “traced the biological response to acidified surface waters” (5). Independent geochemical proxies of carbonate ion saturation are required to first identify intervals of surface water acidity before biotic response is investigated. It is noteworthy that at the Paleocene Eocene Thermal Maximum (~56 million years ago), there is wide-

spread evidence of deep-sea carbonate dissolution (10) and possible surface ocean carbonate saturation change (11) but no convincing evidence that surface water carbonate chemistry changes had a major impact on the calcifying plankton [see discussion in (12)].

Our second concern is that the study sections described by Erba *et al.* (5) comprise diagenetically modified limestones and black shales, yet the effects of variable carbonate preservation on the records are not addressed. Carbon-rich sediments have CO_2 -rich, acidic pore waters that lead to postdepositional dissolution and mobilization of carbonate that affect both nannofossil and geochemical records. The interpretation of ~2 to 3 per mil (‰) excursions in bulk oxygen isotopes as multiple, short-lived (~10,000 years) warming and cooling events is debatable when the diagenetic history is clearly complex. Although primary long-term $\delta^{18}\text{O}$ trends may be recorded by such limestones (13), high-resolution records through variable lithologies may be strongly modified by diagenesis, leading to $\delta^{18}\text{O}$ patterns bearing little or no resemblance to the original seawater signal (14, 15).

Third, modeling studies of ocean acidification indicate that only rapid releases (<10,000 years) of large amounts of carbon into the ocean-atmosphere cause a substantial drop in surface ocean pH and carbonate saturation state (11). However, quantifying the magnitude and rate of CO_2 pulses during OAE1a is problematic due to the reliability of age models on sub-Milankovitch time scales, the difficulty of quantifying contributions from various sources of carbon, and the competing effects of carbon release and burial. Such constraints are required to assess the feasibility of surface ocean acidification during the onset of OAE1a. Additionally, the sequence of surface and deep-ocean acidification must be realistic. Erba *et al.* (5) suggest a delay of 25,000 to 30,000 years between acidification in the surface and deep ocean, but modeling of current and past climate scenarios requires a coupling of surface and deep-ocean carbonate chemistry on the order of the ocean mixing time (~1000 years) (11).

We conclude that although there was undoubtedly a biotic response to environmental changes during OAE1a, there is no compelling evidence that surface ocean acidification was the dominant control on nannoplankton assemblages or coccolith morphology. Any primary ecological or geochemical signals have likely been modified by diagenesis, and we question the use of nannofossil accumulation rates as a proxy for primary carbonate production in these sediments. To robustly discuss the biotic effects of ocean acidification in the geological record, independent proxy records or models must be available that constrain both the rate and magnitude of changes in surface ocean carbonate chemistry. Such estimates are not currently available for OAE1a, making discussion of the biotic record in terms of ocean acidification premature.

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