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## CO2-concentrating mechanisms, harmful blooms, and Late Devonian reef extinction 375 million years ago

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Late Devonian Mass Extinction caused the largest change experienced by reef biotas in the entire Phanerozoic. Stromatoporoid-coral communities that had dominated metazoan reefs since the mid-Ordovician disappeared. In the extinction's immediate aftermath they were replaced by microbial reefs. By the Early Mississippian rimmed shelves had given way to ramps dominated by carbonate mud mounds. The Mass Extinction selectively eliminated shallow marine organisms, including acritarch phytoplankton as well as reef biotas.

Here I suggest induction of CO2-concentrating mechanisms (CCMs) in marine phytoplankton as a factor in Late Devonian Mass Extinction. CCMs help maintain photosynthesis when levels of dissolved inorganic carbon are low. Late Devonian decline in atmospheric CO2 level was sufficient to induce CCMs in aquatic algae and cyanobacteria. This is likely to have had several geologically recognizable effects. Firstly, CCMs promote phytoplankton productivity and bloom conditions by helping to overcome carbon limitation. Productivity enhances organic matter burial, and harmful blooms kill shallow-water reefs and pelagic organisms. Secondly, conditions favouring photosynthetic groups with effective CCMs can promote community restructuring, resulting in extinction of some phytoplankton groups. Thirdly, cyanobacterial CCMs can stimulate calcification, both in the water column as 'whitings', and in benthic mats as in situ microbial carbonates.

The Late Devonian marine realm underwent marked changes in addition to Mass Extinction. Organic carbon-rich sediments, microbial carbonates, and carbonate mud mounds significantly increased in abundance. These, at first sight disparate, developments all have potential links to CCM induction in phytoplankton. Harmful blooms could have contributed to extinction of shallow marine metazoans, and increased phytoplankton productivity would have increased organic carbon-rich sediments. Phytoplankton community restructuring could have led to acritarch extinction. Combination of increased microbial productivity and enhanced cyanobacterial calcification would have promoted both microbial carbonate and carbonate mud mound development. These possibilities do not exclude the likely involvement of additional causative factors.