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Microbial exoenzymes promoted the transition to an oxygenated Earth

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Heterotrophic microorganisms are central to the cycling of carbon, nitrogen, and phosphorus on Earth by mediating the remineralization of organic matter. Here, we investigate the evolutionary history of microbial extracellular enzymes ("exoenzymes") that initiate the breakdown of complex organic matter, thereby influencing both carbon burial and nutrient recycling, two fundamental levers on planetary oxygenation. We quantified the genomic distribution of exoenzymes across microbial metabolisms to assess how changing environmental redox conditions shaped their prevalence in ancient oceans. To place these patterns in an ecological context, we used a marine carbon cycle model to explore changes in particulate organic matter, which favor exoenzyme production. We further used molecular clock analyses to constrain the timing of extracellular alkaline phosphatase, a key exoenzyme involved in the hydrolysis of organic phosphorus compounds.

Our results show that exoenzymes are concentrated in metabolic groups that use more energetically favorable electron acceptors. This indicates that redox state has not only shaped the occurrence of microbial metabolisms but also the extent and efficiency of carbon burial and nutrient regeneration over geological time. Our modelling results found that early Archean oceans offered few particulate-rich habitats, as low productivity and intense photodegradation kept particulate organic matter concentrations low. Following the rise of oxygen in the Paleoproterozoic, the development of a protective ozone layer, coupled with increased primary productivity, expanded particle-rich habitats where exoenzymes confer a selective advantage. In parallel, rising oxygen levels increased the availability of energetically favorable electron acceptors, supporting the expansion of exoenzyme-producing microbial groups and enhancing nutrient regeneration. Consistent with this ecological shift, molecular clock analyses show that extracellular alkaline phosphatase likely emerged between the Neoarchean and Paleoproterozoic. We propose that the evolution of exoenzymes initiated a positive feedback loop: accelerated nutrient regeneration fueled cyanobacterial productivity and oxygen release, which in turn favored greater exoenzyme capacity, reinforcing long-term oxygenation of the planet. Together, these findings support a framework in which planetary oxygenation reflects coupled changes in microbial producers and consumers within an evolving environment.