

Exploring Early Earth's Oceanic Oxygenation: Geochemical Insights from Case Studies

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Geological records reveal numerous oceanic oxygenation events in Earth's history, yet their nature and causes remain poorly understood. Understanding these events is crucial for elucidating how Earth's oceanic environment evolved from early anoxia to today's well-oxygenated state and for understanding the conditions under which early complex life evolved. Oxygenation in the ancient oceans typically fits into two modes: localized oxygen oases due to local oxygenic photosynthesis, common in anoxic oceans amidst little or no atmospheric oxygen, such as in the Archean, and global oceanic oxygenation facilitated by elevated atmospheric oxygen levels through water-atmosphere exchange. The Neoproterozoic records a pivotal shift in atmospheric-oceanic oxygen levels from low to high, during which both types of oxidation patterns may have existed, but distinguishing between them is challenging. Integrated geochemical investigations, utilizing proxies reflecting local redox conditions, global oxidation levels, or tracing oxygen sources, may offer solutions. Here, we present two case studies to delve into this issue: 1) Integrated geochemical analyses (including Fe speciation, trace metals, and sulfur isotopes) of the Tonian Longfengshan Biota-bearing strata reveal oxic bottom waters associated with predominantly anoxic water-column conditions. This suggests a localized oxygen oasis regulated by the benthic macroalga Longfengshaniaceae and/or microbial mats, which contributed to oxidative power in reducing environments. It is further speculated that benthic oxygen oases may have been common in redox-stratified Proterozoic oceans until the euphotic zone became well-oxygenated. 2) Sulfate triple oxygen isotopes were employed to unravel oxygen sources during the late Ediacaran Shuram Event, a large negative excursion in inorganic carbon isotopes widely interpreted as a consequence of oceanic oxygenation. Notable is a large ¹⁷O depletion in sulfate oxygen during the Shuram, a diagnostic signal exclusively derived from atmospheric oxygen in nature (this signal is largely absent in strata above and below the Shuram). This finding confirms the Shuram as a global oceanic

oxygenation event linked to an increased supply of atmospheric oxygen. These studies provide evidence for a transition of oceanic oxygenation modes from the early to the late Neoproterozoic and shed light on their relationships with the contemporaneous evolution of early complex life.