Redox state of the marine nitrogen cycle and evolution of eukaryotes during late Neoproterozoic

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The oxidation state of fixed nitrogen (N), a major limiting nutrient for marine primary production, is dictated by the ambient environmental redox conditions: in an anoxic ocean, inorganic N would be stable as ammonium, while in the presence of dissolved O_2 nitrate is stable. We have developed a method of determining nitrate content in carbonates, Carbonate Associated Nitrate (CAN), as a proxy for the oceanic nitrate content. To investigate changes in the global O_2 and marine nitrogen cycles through time, concentrations of CAN have been evaluated in both limestones and dolostones from multiple localities around the world, spanning the ages from ~3 Ga through modern. The highest CAN values were found as several distinct peaks in the late Neoproterozoic carbonates from two locations: Caborca in Sonora, Mexico, within a stratigraphic sequence deposited during the Ediacaran, and within the Rainstorm Member of the Johnnie Formation in the Death Valley, California, likely deposited at the onset of the Ediacaran Shuram $\delta^{13}C$ excursion. The $\delta^{15}N$ of nitrate in these rocks is consistent with oxidation of the pre-existing oceanic ammonium pool, perhaps driven by increasing pO_2 during this time. Transformation of fixed N from the reduced to the oxidized form (from ammonium to nitrate) may have caused a major restructuring of the global ocean N cycle, potentially contributing to the diversification of the eukaryotic phytoplankton, which were forced to adapt to nitrate instead of ammonium as the major nitrogen source.