The geologic history of marine dissolved organic carbon from iron oxides

Nir Galili[1], Stefano M. Bernasconi[1], Alon Nissan[2], Uria Alcolombri[2,3], Giorgia Aquila[1], Marcella Di Bella[4], Thomas M. Blattmann[1], Negar Haghipour[1,5], Francesco Italiano[6], Madalina Jaggi[1], Ifat Kaplan-Ashiri[7], Maxwell A. Lechte[8], Susannah M. Porter[9], Maxim Rudmin[10], Robert G.M. Spencer[11], Stephan Wohlwend[1], **Jordon D. Hemingway**[1]

[1]Geological Institute, Department of Earth Sciences, ETH Zurich, Zurich, Switzerland
[2]Institute of Environmental Engineering, Department of Civil, Environmental, and Geomatic Engineering, ETH Zurich, Zurich, Switzerland
[3]Institute for Life Sciences, Department of Plant and Environmental Sciences, The Hebrew University of Jerusalem, Jerusalem, Israel
[4]National Institute of Oceanography and Applied Geophysics, Sgonico, Italy
[5]Laboratory of Ion Beam Physics, ETH Zurich, Zurich, Switzerland
[6]National Institute of Geophysical and Volcanology, Palermo, Italy
[7]Department of Chemical Research Support, Weizmann Institute of Science, Rehovot, Israel
[8]Department of Earth and Planetary Sciences, McGill University, Montreal, Canada
[9]Department of Earth Science, University of California, Santa Barbara, Santa Barbara, USA
[10]Division for Geology, Tomsk Polytechnic University, Tomsk, Russia
[11]Earth, Ocean, and Atmospheric Science, Florida State University, Tallahassee, USA

Dissolved organic carbon (DOC) is the largest reduced carbon reservoir in modern oceans. Its dynamics regulate marine communities and atmospheric CO_2 levels, whereas ^{13}C compositions track autotrophic metabolism. However, the geologic history of marine DOC remains entirely unconstrained, hindering our ability to mechanistically reconstruct coupled ecological and biogeochemical evolution. To address this, we developed the first direct proxy for past DOC signatures using co-precipitated organic carbon in iron ooids, and we applied this to 26 marine iron ooid-containing formations deposited over the past 1650 million years. Predicted DOC concentrations were near modern levels in the Paleoproterozoic then decreased by 90-99% in the Neoproterozoic before sharply rising in the Cambrian. We interpret these dynamics to reflect three distinct states: (i) small, single-celled organisms combined with severely hypoxic deep oceans; (ii) larger, more complex organisms and little change in oxygenation; (iii) continued organism growth and a transition to fully oxygenated oceans. Furthermore, modern DOC is significantly ^{13}C-enriched relative to the Proterozoic, likely due to changing autotrophic fractionation driven by biological innovation; together with isotopically invariant carbon inputs to Earth's surface, this implies increasing relative organic carbon burial through time. Our results reveal new connections between the carbon cycle, ocean oxygenation, and the evolution of complex life.