

Carbonates of the 2.0 Ga Zaonega Formation: REE and Sr isotopic indications of their origin

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The Paleoproterozoic Zaonega Formation, Onega Basin, Russian Karelia represents a deep-water, mixed siliciclastic-carbonate depositional system in a magmatically active basin. It is characterized by rocks extremely enriched in organic matter. FAR-DEEP drillholes intersecting Zaonega Formation hold lithological evidence for one of the earliest generations and spilling of oil/asphalt onto the sea floor, with part of the hydrocarbons being generated due to syn-sedimentary magmatic activity. Geochronologic maximum-minimum constraints of 2.09 ± 0.07 and 1.98 ± 0.02 Ga for the Zaonega Formation indicate its deposition partially overlapped with and/or post-dated the 2.22-2.06 Ga Lomagundi-Jatuli positive carbon isotope interval.

High $\delta^{13}\text{C}_{\text{carb}}$ (up to +10 ‰) suggest that the Zaonega Formation records the end of the Lomagundi-Jatuli Event. However, synsedimentary magmatic activity, and petroleum generation together with extensive post-depositional alteration of carbonates, poses challenges in using these carbonates for interpretations of global environmental changes.

We report new data to assist with interpreting the conditions under which the carbonates precipitated. Carefully characterized carbonate samples were analyzed for REE and Sr isotopes. High $^{87}\text{Sr}/^{86}\text{Sr}$ ratios suggest alteration by post-depositional fluids. Variable REE profiles and changes in magnitude of the Eu anomaly imply that most carbonates were considerably influenced by hydrothermal fluids, but carbonates with sea-water geochemical characteristics are also present. *in situ* REE data show that this complexity is visible both in possibly primary and clearly later carbonate phases and that hydrothermal fluids were important during some carbonate precipitation and during later burial. Contribution from organic diagenesis remains to be evaluated. Whole rock data from these rocks should be therefore viewed cautiously with respect to assessing the Paleoproterozoic carbon cycle.

Reactive Oxygen Species (O_2 , O_2^- and H_2O_2) control Manganese redox cycling in the euphotic zone: role of reactive intermediates

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Manganese (Mn) is an essential element for oceanic phytoplankton as it plays a critical role in photosynthesis, through its unique redox chemistry, as the active site in photosystem II and in enzymes that act as defences against reactive oxygen species (ROS), most notably for protection against superoxide (O_2^-), through the action of superoxide dismutase (SOD), and against hydrogen peroxide (H_2O_2) via peroxidases and catalases. The distribution and redox speciation of Mn in the ocean is also strongly controlled by reactions with ROS. Here we examine the connections between ROS and dissolved Mn species in the upper ocean using a combination of field data from the Tropical Pacific and Atlantic, with laboratory data under controlled conditions. We find that reactions with Mn are a significant pathway for the dismutation of O_2^- in the Tropical Atlantic in surface waters where Mn concentrations are elevated due to Saharan dust input. Modelling of our data suggest it is unlikely that significant concentrations of Mn(III) are produced in the euphotic zone, as in the absence of evidence for the existence of strong Mn(III) ligands in seawater, Mn(II) reacts with O_2^- to form the short lived transient manganese superoxide, MnO_2^+ , which may react rapidly with other redox species in a similar manner to O_2^- . Experiments with the strong Mn(III) chelator, desferrioxamine B (DFB), in seawater indicated that Mn(III) species are unlikely to form significant concentrations via oxidation of the the pre-cursor Mn(II) complex, as this species is only a minor species under natural ambient conditions due to the high side reaction of DFB with Ca.