

# Mesoproterozoic upwelling-induced spatial and temporal redox heterogeneity of the Hongshuizhuang Formation, North China

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The evolution of ocean chemistry during the Mesoproterozoic Era (1.6-1.0 Ga) is thought to influence the rate of eukaryote revolution. Changes in oxygen content and nutrients have been the subject of longstanding debate. Several kilometers thick of marine carbonates dominated the Early Mesoproterozoic Era (1.6-1.4 Ga) in the Yanliao Basin on the North China Craton but black shales were discovered in the Hongshuizhuang Formation exhibiting high TOC contents. This transition indicates a major upheaval in ocean chemistry, but the precise nature of this change remains unsolved. Here, we present high-resolution Fe speciation-trace element geochemical records from the YJ-2 well of the Yanliao Basin to reconstruct bottom-water redox conditions, integrating these results with previously published data from four sections representing a range of water depths (Jixian section, Qinghe section, JQ-1 well, CQ-1 well). Redox states of drillholes or sections at different locations show inconsistent redox dynamic evolution throughout the Hongshuizhuang Formation. Integrated productivity proxies (TOC, Cu/Al, and Ni/Al) and depositional system ((Mo/U)<sub>auth</sub>, Co×Mn and Co<sub>EF</sub>×Mn<sub>EF</sub>, enrichment factors of trace metals) data reflect that productivity levels varied during deposition of the Hongshuizhuang Formation, with high productivity in the Lower-Middle Hongshuizhuang Formation fueled mainly by open-sea upwelling. Thus, stratified redox models with time were developed in consideration of both spatial redox heterogeneity and upwelling events. Furthermore, a nitrogen cycling process was proposed under a Fe(II), anoxic upwelling zone to show how the sedimentary environment affected the nitrogen isotope ( $\delta^{15}\text{N}$ ) compositions from the Lower to Middle Hongshuizhuang Formation. In an upwelling system, the positive  $\delta^{15}\text{N}$  excursion is attributed to denitrification in ferruginous conditions during the Lower Hongshuizhuang Formation to the lower part of the Middle Hongshuizhuang Formation. The positive  $\delta^{15}\text{N}$  values are nearly constant in the upper part of the Middle Hongshuizhuang Formation. This condition implies that dissimilatory nitrate reduction to ammonium (DNRA) dominances  $\text{NO}_3^-$  reduction to  $\text{NH}_4^+$  without  $^{14}\text{N}$  lost to the atmosphere in the euxinic condition.