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Surface reactivities of biogenic ferrihydrite aggregates formed during oxygenic photosynthesis: a look into the trace element cycling in ancient oceans from a surface adsorption perspective

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Precambrian banded iron formations (BIF) are iron- and silica-rich chemical sedimentary rocks that are commonly used as paleo-redox proxies. Oxidation of dissolved Fe(II) was partially caused by oxygen produced by cyanobacteria to form a metastable and amorphous mineral phase ferrihydrite, $Fe(OH)_3$. Cyanobacterial cells and ferrihydrite tend to aggregate due to opposite surface charges at seawater pH, both with or without the presence of dissolved Si. However, to date, there has been no systematic characterization of the combined surface reactivity of those aggregates formed under predicted Precambrian seawater conditions. To fill this knowledge gap, we formed both silica-spiked ferrihydrite and cyanobacteria-ferrihydrite aggregates *in situ* and then conducted empirical potentiometric acid-base titrations and Cd adsorption experiments on the fresh aggregate samples at three different ionic strengths (0.56 M, 0.1 M and 0.01 M). We intentionally minimized sample processing (i.e., drying and powdering) to a simple washing step, in which the aggregate pellets remained hydrated, because both amorphous silica and ferrihydrite can be easily transformed, thus altering their true surface reactivity in seawater. Experimental results were then fitted with diffuse-double-layer model at different ionic strengths to better predict both surface charges and metal-adsorption behavior of ferrihydrite aggregates. Preliminary result shows that the surface reactivity and Cd adsorption capacity of cyanobacteria-ferrihydrite aggregates differs from their individual components, especially over the predicted Precambrian seawater pH 6 to 8. This discrepancy suggests that biogenic ferrihydrite aggregates do not have additive surface reactivity, a fact which needs to be taken into consideration in order to predict trace element adsorption to the surface of the aggregates and ultimately in understanding the trace element archive of the sedimentary rocks used to reconstruct Precambrian ocean chemistry.