Using a novel approach to characterize the surface reactivities of silica-rich ferrihydrite and biogenic cyanobacteria-ferrihydrite aggregates and the implications for Archean ocean geochemistry

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Abstract

Precambrian banded iron formations (BIF) are iron- and silica-rich chemical sedimentary rocks that are commonly used as paleo-redox proxies for Archean and Paleoproterozoic seawater geochemistry. At the onset of the Great Oxidation Event (herein GOE) around 2.4 Ga, cyanobacteria flourished with increasing nutrient fluxes due to oxidative weathering on land. In turn, this led to increased primary productivity that facilitated the permanent shift from a reducing Earth atmosphere to an oxidizing one. Interestingly, the duration of GOE also overlapped with one of the most prolific periods of BIF deposition.It is widely accepted that cyanobacteria were likely responsible for BIF formation during the GOE. Oxidation of dissolved Fe(II) by oxygen produced from cyanobacteria forms a metastable and amorphous mineral phase ferrihydrite, $Fe(OH)_3$. As an essential component in both ancient BIF deposits and various modern ecosystems, the surface reactivity of ferrihydrite has been extensively studied under different conditions (i.e., pH and ionic strengths). Not only are the highly reactive surfaces of ferrihydrite particles important shuttles for trace element transport from the water column to the sediment pile, but previous studies have also demonstrated that cyanobacterial cells and ferrihydrite tend to aggregate at seawater pH. This means that ferrihydrite was also a vector for the transport of organic carbon to the seafloor. However, a complicating issue is how co-ions affect the surface reactivity of ferrihydrite, specifically dissolved silica which was abundant in ancient seawater. Although previous studies have demonstrated that silica can passivate the surface reactivity of ferrihydrite, what remains unclear is how silica impacts ferrihydrite-biomass aggregation.

To fill this knowledge gap, we formed both silica-spiked ferrihydrite and cyanobacteria-ferrihydrite aggregates *in situ* and subsequently 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 minimized sample processing (i.e., drying and powdering) to a simple washing step, in which the aggregate pellets remained hydrated to avoid any mineral transformation thus altering their true surface reactivity in seawater. Experimental results were then fitted with non-electrostatic model to predict both surface charges and metal-adsorption behavior of ferrihydrite aggregates. Different from previous surface-complexation modelling studies, here we used a novel and more powerful modelling program called Phreefit. It utilizes the global optimization algorithms instead of more commonly used Newton-Raphson method in FITEQL program, which is often too limited for precisely modelling complex systems such as the two samples in this study. Furthermore, we also measured the surface charges of both samples over the pH range from 3 to 9 on a Malvern Zetasizer and characterized the surface functional groups through Fourier-Transform Infrared Spectroscopy to help with our interpretation of the experimental data.Preliminary results show that cyanobacteria-ferrihydrite aggregates formed primarily due to ionic bridging. Cyanobacterial cells likely facilitated the precipitation of dissolved silica. Findings from titration and Cd adsorption experiments indicate that the surface reactivity and capacity of both silica-rich ferrihydrite cyanobacteria-ferrihydrite aggregates to adsorb trace elements differ from their individual components, likely due to site blockage. This distinction is particularly prominent when considering the expected Archean seawater pH from 6 to 8. This disparity implies that the biogenic ferrihydrite aggregates do not exhibit an additive surface reactivity, which is in agreement with similar previous studies. Our combined results are crucial to accurately predict the adsorption of trace elements onto the aggregate surface and, ultimately, comprehend the archive of trace elements in sedimentary rocks used to reconstruct Precambrian ocean chemistry.

Keywords

Banded Iron Formation; Cyanobacteria; Surface complexation modelling

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Conflicts of interest

The authors have declared that no competing interests exist.