

Depositional setting and biological activity highlighted by Cr concentration, 3.2 Ga Moodies Group, Barberton Greenstone Belt

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Previous studies suggest that atmospheric oxygen increased by emergence of cyanobacteria at 2.45 Ga Great oxidation event (GOE). Fluctuation of microbial activities prior to prosperity of cyanobacteria and oxidation state might be expected in shallow ocean before GOE. 3.2 Ga Moodies Group, Barberton Greenstone belt, South Africa, is focused as a significant archive of shallow ocean environment before GOE which consists of detrital sedimentary rocks including Banded Iron Formations (BIFs), chemical deposits associated with microbial activities in terms of the Fe oxidation process. In such a transitional environment, behavior of redox-sensitive elements can be important factors to evaluate oxidation state. In this study, we performed detail observation of Cr-bearing minerals as an indicator of redox state together with geological, petrological and geochemical investigation to understand fluctuation of depositional setting and biological activity on 3.2 Ga shallow BIFs of Sheba gold mine, Moodies Group.

Rock samples were classified into Sandy-siltstone (6.1–16.3 wt% Fe₂O₃), Carbonate rich (Carb-) siltstone (21.6–32.8 wt% Fe₂O₃) and Magnetite rich (Mgt-) siltstone (18.9–50.2 wt% Fe₂O₃) based on petrographic observations. Modal analysis indicates that grain size ratio of <30 : > 30 (μ m diameter) without chemical precipitates are almost identical in all rock types, suggesting they deposited at identical sedimentary depth although Fe host minerals are different from each other (Sandy- and Carb-siltstone: carbonate and silicate, Mgt-siltstone: magnetite). Contents and stable isotope ratios of organic carbon in these samples indicate 0.03–0.29 wt% and \sim –27 per mil, suggesting the biogenic origin. Carbon stable isotope ratio of carbonate ranges –12.5 to –3.4 per mil, which indicates isotopic contribution of organic carbon to carbonate. Morphologies of organic materials extracted by acid-treatment are classified into three types: 30–50 μ m flake, > 100 μ m filament and \sim 50 μ m indeterminate grain. Carb-siltstone is rich in filaments compared to Mgt-siltstone although Carb-siltstone and Mgt-siltstone deposited in identical sedimentary settings. The result suggests multiple microbial species and fluctuation of the microbial activities in 3.2 Ga shallow oceans.

Host mineral of Cr is \sim 50 μ m chromite surrounded by magnetite in Mgt-siltstone, on the other hand, chromite is rare in Sandy- and Carb-siltstone and it is not accompanied by magnetite. Point counting of thin sections indicates that Mgt-siltstone contain \sim 60-130 chromite grains/cm², whereas Sandy and Carb-siltstone contain < 20 chromite grains/cm², although bulk Cr concentrations are almost identical (Mgt-siltstone: 166-1341ppm, Sandy- and Carb-siltstone: 455-1449ppm). FE-EPMA analysis showed that main host minerals of Cr in Sandy- and Carb-siltstone are biotite and chlorite which contain 1.22 ± 0.66 wt% and 1.54 ± 0.58 wt% Cr₂O₃ respectively, whereas biotite and chlorite in Mgt-siltstone contain 0.26 ± 0.40 wt% Cr₂O₃. The variation of Cr host minerals coupled with rock facies cannot be explained by simple Cr source such as detrital chromite supply from weathered igneous rocks under anoxic condition. Our results suggest Cr⁶⁺ was dissolved in 3.2 Ga shallow oxic ocean and distributed to silicate or concentrated in magnetite during early diagenesis after coprecipitation with iron hydroxide. Bulk Cr/TiO₂ ratio showed positive correlation with Fe₂O₃/TiO₂ ratio in all rock types and high values in Mgt-siltstone, which also supports coprecipitation of Cr and Fe.

In summary, our data indicates that fluctuation of multiple microbial activities and subsequent changes of mineral assemblages including host minerals of Fe and Cr in 3.2 Ga shallow ocean: when microbial

activities were low, iron hydroxide coprecipitated with Cr ($\text{Cr}^{6+} + \text{Fe}^{2+} + 3\text{OH}^- \rightarrow \text{Cr}^{3+}, \text{Fe}^{3+} (\text{OH})_3$) at the redox boundary and converted to magnetite-chromite during early diagenesis. When microbial activities were high, iron hydroxide coprecipitated with Cr and converted to carbonate using parts of organic carbon buried together during early diagenesis. Cr was then distributed to surrounding biotite and chlorite due to the lack of the available sites in crystal structure of carbonate.

Keywords: Moodies Group, Chromite, Organic matter