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# Fe isotope signatures for oxidative precipitation of ferrous iron in ~3.2 Ga shallow ocean from the Moodies Group, Barberton Greenstone Belt, South Africa

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Iron isotopic signatures in Banded Iron Formations (BIFs) have the potential to provide information on ocean chemistry and evolution of marine biosphere on early Earth since they may preserve their biological or abiological formation pathways. However, there are controversies regarding interpretations of variable Fe isotope values recorded in BIFs, such as iron sources, the reaction in the seawater or the effect of microbial activity during sediment burial. In this study, we focus on BIF that was deposited in a shallow ocean in the lower section (MdS1) of the ~3.2Ga Moodies Group in the Barberton Greenstone Belt, South Africa. The $\delta^{56}$Fe values were variable from -0.58 to +0.60‰ in different groups of rock samples (i.e., magnetite-rich, carbonate-rich, and clastic sedimentary rocks). The whole rock $\delta^{56}$Fe values in magnetite-rich and carbonate-rich groups tend to decrease with decreasing the Fe/Ti ratios as well as shallowing the depositional environments. No significant difference was observed in the trend between the two groups. These results indicate that the variation in the bulk Fe isotopes record the chemical precipitation process of ferrous iron supplied from the deep ocean, possibly from a hydrothermal fluid, following a Rayleigh fractionation-type model. Furthermore, Fe isotope fractionation during the formation of Fe(ll)-silicates (e.g., greenalite), which have recently been proposed as a primary Fe mineral in BIFs, was also examined by synthetic experiments. The experimental results suggest that oxidative precipitation of ferrous iron to precipitate Fe(lll) mineral (e.g., ferrihydrite), not Fe(ll)-silicates, governs the observed variations in the bulk $\delta^{56}$Fe values in the BIF. Although the primary Fe(lll) mineral transformed to Fe(ll)-bearing minerals (e.g., magnetite and ankerite) after the deposition coupled with oxidation of organic carbon, the mobility of reduced iron was likely limited during diagenesis. Therefore, the Fe isotope signatures reflecting processes occurred in a water column were preserved in the BIF in Moodies Group.