

Iron isotope fractionation in the 3.2Ga Moodies Banded Iron Formations, Barberton Greenstone Belt, South Africa

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Iron isotopic signatures in Banded Iron Formations (BIFs) have the potential to provide information about the ocean chemistry and evolution of the marine biosphere on early Earth since they may preserve their biological or abiological formation pathways. However, there are controversies on interpretations of variable iron isotope values recorded in BIFs, such as progressive partial oxidation of hydrothermal fluids following a Rayleigh fractionation-type model or the effect of microbial dissimilatory iron reduction (DIR). In this study, the lower section (MdS1) of the Moodies BIFs, which were deposited in a shallow ocean, including detrital components from the continent, at ~3.2Ga in Barberton Greenstone Belt, South Africa are focused on. Novel relationships of the whole rock Fe isotope data ($\delta^{56}\text{Fe} = -0.58$ to $+0.56\text{‰}$) with iron contents and sedimentary environments of different groups of rocks (i.e., magnetite-rich, carbonate-rich, and clastic sedimentary rocks) are presented. The bulk $\delta^{56}\text{Fe}$ values ($\delta^{56}\text{Fe} = -0.54$ to $+0.56\text{‰}$) in magnetite-rich and carbonate-rich groups, which contain much iron from chemical precipitations, tend to increase with increasing of iron contents and as go deeper in the depositional environments. A significant difference in the trend was not observed between magnetite-rich and carbonate-rich groups. These results indicate that the variation in the bulk Fe isotopes reflects precipitation process of a same precursor following a Rayleigh fractionation-type model. Furthermore, Fe isotope fractionation during the formation of Fe(II)-silicates (e.g., greenalite), which have recently been proposed as the primary Fe mineral in BIFs, was also examined by the synthetic experiments. The results demonstrate that the Fe isotope fractionation between Fe(II)-silicates and $\text{Fe}^{2+}(\text{II})$ is too small to satisfy the measured range of observed $\delta^{56}\text{Fe}$ values in the Moodies BIFs. Since oxidative precipitation of dissolved ferrous iron as ferric (Fe(III)) hydroxide (e.g., ferrihydrite) is known to cause large Fe isotope fractionations, the observed variation of $\delta^{56}\text{Fe}$ values can be only explained by the formation of ferric hydroxide as the primary precipitate. Although ferric hydroxide was transformed, possibly DIR involved, to secondary Fe(II)-bearing minerals, such as magnetite and siderite, via the oxidation of microbial organic carbon, the Fe isotope signatures reflecting the precipitation process following a Rayleigh fractionation-type model were likely preserved in the geological record of the Moodies BIFs.

Keywords: Earth history, isotope, sedimentary rock, microorganism, iron, oxygen