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Mesoarchean pO2 and pCO2 based on REE and oxygen isotope geochemistry of BIF from Barberton, South Africa

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A popular mechanism for BIF (Banded Iron Formation) deposition is that Fe-oxides were precipitated in deep-water setting by oxidation of dissolved Fe^{2+} supplied from submarine hydrothermal activity, by dissolved oxygen supplied from oxygenic photosynthesis in the surface ocean. When Fe-oxides precipitated, rare earth elements (REEs) were adsorbed on their surface. REE compositions of seawater have been recognized to reflect redox state of seawater and the extent of input from hydrothermal activity. In this study, we aimed to estimate Mesoarchean seawater chemistry and temperature based on REE signatures of 3.2 Ga old BIFs. These are directly related to pO_2 and pCO_2 in the Mesoarchean atmosphere.

Samples were collected from outcrops of the Mapepe Fm at the bottom of the Fig Tree Group and Msauli Member in the Onverwacht Group, both belonging to the Swaziland Supergroup. Powdered rock samples were analyzed for their major element, REE, and oxygen isotope compositions. Samples with $<$0.5 wt.% Al_2O_3 are considered to be pure chemical precipitates and thus used for further discussion.

Chondrite-normalized REE patterns of the Mapepe samples show positive Eu anomaly, elevated Y/Ho ratios, and LREE$>$HREE. Furthermore, there exist positive correlations among the extent of positive Eu anomaly, $\sum Fe_2O_3$ contents, and Y/Ho ratios. The maximum Y/Ho ratios are surprisingly comparable to those of the modern ocean. These characteristics suggest a coherent story for BIF deposition; Fe^{2+} emanated from submarine hydrothermal activity was oxidized to Fe^{3+}, which, with enhanced particle reactivity, absorbed dissolved REEs and Y in the 3.2 Ga ocean, producing elevated near-modern Y/Ho ratios. The Msauli samples are mostly enriched in Al_2O_3 and have clastics-dominated REE patterns, suggesting deposition at shallower, more proximal setting.

We also estimate temperature of seawater 3.2 Ga ago from which the BIF precipitated to be around 60-70 ℃, based on their oxygen isotope compositions of silicate- and Fe-oxide phases and their binary mixing model. Although crustal heat flux at that time was most likely higher than today, the pCO_2 in the Mesoarchean atmosphere should have been high enough to warm up the seawater under faint young Sun. The pO_2 in the Mesoarchean atmosphere should have been high enough to oxidize dissolved Fe^{2+} supplied from submarine hydrothermal activity.

Keywords: Archean, BIF, REE, Oxygen isotope, South Africa