

Marine Environments 3.2 Ga ago: Constraints from REE Geochemistry of BIF/Chert in Barberton, South Africa.

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Banded iron formation (BIF), a chemical sediment interbedded with iron and silica, characteristically exists in the early history of the Earth. A popular mechanism for BIF deposition is that Fe-oxide was precipitated in deep-water setting by oxidation of dissolved Fe²⁺ supplied from submarine hydrothermal activity by dissolved oxygen supplied by oxygenic photosynthesis in the surface ocean. When Fe-oxide precipitated, phosphorus and rare earth elements (REEs) were adsorbed on its surface. REE compositions of seawater have been recognized to reflect redox state of seawater and the extent of the contribution of hydrothermal activity. In this study, we aimed to estimate Mesoarchean seawater chemistry based on REE signatures of 3.2 Ga old BIFs in the northeastern part of the Barberton Greenstone Belt, South Africa.

Samples of this study were collected from the outcrop of the Mapepe Formation 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 compositions using XRF at the University of Tokyo and REE compositions using ICP-MS at Japan Chemical Analysis Center. The samples are essentially two-component system composed of silica and Fe-oxide (SiO₂+total Fe₂O₃ = ~100%). Samples with <1.0 wt% Al₂O₃ are considered to be "pure chemical precipitates" and thus used for further discussion.

Chondrite-normalized REE patterns show positive Eu anomaly and LREE > HREE, suggesting significant influence of syn-depositional hydrothermal activity. Decoupling of Y-Ho, most likely due to difference in adsorption capacity onto precipitating Fe-oxide particles, suggests precipitation of Fe-oxide. Positive correlations between Y/Ho ratios and total Fe₂O₃ contents and between Y/Ho ratios and degree of Eu anomaly coherently suggest the following scenario; dissolved Fe²⁺ of hydrothermal in origin was oxidized to Fe-oxides, which preferentially adsorbed Ho over Y. The Y/Ho ratios of seawater were progressively increased, and so did those of BIFs. Strong negative Ce anomaly, typically observed in the oxic ocean, was not observed. This is probably due to either (1) the elevated mixing ratio of hydrothermal fluids to oxic seawater that could have had negative Ce anomaly, or (2) seawater did not contain significant amount of dissolved oxygen to develop negative Ce anomaly. Now we are measuring oxygen isotope compositions of BIF/chert samples to estimate mixing temperature and mixing ratios of seawater to hydrothermal fluids.

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