

Rare earth element geochemistry of 3.2 Ga BIF/chert from Pilbara, Western Australia, and Barberton, South Africa.

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Introduction: Banded iron formations (BIFs) are chemical sediments interbedded with Fe- and Si-rich layers, characteristically present in the early history of the Earth. A popular hypothesis for the formation of BIFs postulates that dissolved oxygen produced by photosynthesizers such as cyanobacteria oxidized dissolved ferrous Fe supplied by submarine hydrothermal activities. During precipitation of Fe-oxide minerals, rare earth elements (REEs) were most likely adsorbed on their surface. Therefore, chemical compositions of REEs that adsorbed onto Fe-oxide have useful information on the seawater chemistry at the time of deposition. Especially, information on the redox state of seawater and the extent of the contribution of hydrothermal activity during BIF deposition are expected to have been recorded. Occurrence of BIF has been traditionally tied to the chemical evolution of the atmosphere. Rise of atmospheric oxygen, or as known as GOE (Great Oxidation Event: e.g., [1]), has been widely believed to have occurred at around 2.4 Ga ago. Contrary, however, some studies have suggested such oxygenation could have occurred earlier (e.g., [2, 3, 4]).

Samples: In this study, we used three sets of 3.2 Ga old BIF/chert samples. They are from the Dixon Island Formation of the Cleaverville Group, Pilbara, Western Australia, the Mapepe Formation of the Fig Tree Group and Msauli Member of the Onverwacht Group in the Barberton Greenstone Belt, South Africa. We aimed to constrain the marine environment, and by inference atmospheric environment, at the time of BIF deposition from REE geochemistry.

Major elements and REE compositions of 30 samples were measured using XRF and ICP-MS, respectively. Samples with less than 1.0 wt% Al₂O₃ are considered to be “pure” BIF/chert with minimal amount of continental contamination, and are expected to have inherited marine REE signatures. Only 6 samples were classified as pure and typical Archean BIF, with Si and Fe dominating the major element abundance.

Results and Discussion: The C1 chondrite (C1C)-normalized REE patterns of the Australian samples exhibit positive Eu and Y anomalies, but don't exhibit negative Ce anomaly. Their Eu/Eu* values of all sam-

ples range from 0.5 to 1.6 (avg. 1.1 ± 0.1) and the Y/Ho ratios range from 40 to 80 (avg. 55 ± 2). South African samples commonly exhibit positive Eu anomaly. These data commonly suggest significant influence of hydrothermal fluid on BIF deposition. Minor but variable degrees of the negative Ce anomaly in both of Australian and African samples suggest a local difference in the redox state at the time of deposition. No significant negative Ce anomaly possibly suggest (1) greater mixing ratios (dilution) of seawater (with negative Ce anomaly) / hydrothermal (no Ce anomaly) during the BIF deposition, or (2) the seawater itself did not possess negative Ce anomaly.

Decoupling of Y/Ho, most likely due to the difference in adsorption behaviour onto Fe-oxide, suggests particle reactivity or precipitation of Fe-oxide. Y/Ho ratios of Australian and African samples show positive correlations with their $\Sigma\text{Fe}_2\text{O}_3$ contents and Eu/Eu* values, strongly suggesting that Fe emanated by hydrothermal venting was oxidized and precipitated as Fe-oxide that adsorbed Y and Ho.

The oxygen isotope compositions of the African samples suggest temperature of fluids where Fe₂O₃ and SiO₂ precipitated to have been ~50-70°C. This temperature range should be regarded as that of 3.2 Ga seawater, not a mixture with hydrothermal fluids, as suggested by a mixing model using Eu/Sm and Sm/Yb ratios of modern seawater and hydrothermal fluid as endmembers.

These characteristics suggest a coherent scenario for BIF deposition; Fe²⁺ emanated from submarine hydrothermal activity was oxidized to Fe³⁺, which, with enhanced particle reactivity, absorbed dissolved REEs and Y in the 3.2 Ga ocean, producing elevated near-modern Y/Ho ratios.

References:

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