Goldschmidt 2000
September 3rd–8th, 2000
Oxford, UK.

Journal of Conference Abstracts
Volume 5(2), 1110

Constraints from REEs on the Processes and Environments for Precambrian Banded Iron Formations: Revaluation of the Data and Models

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Precambrian Banded Iron Formations (BIFs) are the chemical sediments deposited on the seafloor. Their trace elements characteristics are expected to inherit those of the contemporaneous seawater, therefore rare earth elements (REEs) of the BIFs have been used to estimate the chemical characteristics of the ancient oceans. Previous researchers (e.g., Klein and Beukes, 1992) have recognized the existence of prominent positive Eu anomalies and negative Ce anomalies in BIFs. They used such REEs characteristics to support the following model for the BIFs deposition: the Fe-bearing reduced fluids originated as high temperature hydrothermal fluids on mid-oceanic ridges, traveled through an anoxic deep ocean on a bottom current then upwelled to the continental shelf areas, and mixed with shallow, oxygenated water to precipitate Fe oxides. However, some serious problems exist in the previous interpretations of the REEs data of the BIFs. Firstly, the REE values adopted for an end member in their mixing calculations are those of the modern oxic seawater in the mid-depth zone (~2000 m) with a very strong negative Ce anomaly. Shallow ocean water typically shows weak-negative or no Ce anomaly. Secondly, the negative Ce anomalies in BIFs may be artifact of positive La anomalies, because the Ce anomalies were typically quantified by equations using the La and Pr (or Nd) values. (The significance of positive La anomalies in seawater is only recently recognized.) Thirdly, the REE data obtained on Fe-rich samples by the INAA (instrumental neutron activation analysis) method may have large uncertainties, especially for Ce. Fourthly, abnormal REEs patterns in some BIF data may be due to contamination of clastic materials in BIFs. For these reasons, we have examined in detail the REE data on Precambrian BIFs reported in published literatures.

The total number of papers and samples that we have examined are 27 and ~300, respectively; the samples range from 3.8 Ga to 0.7 Ga in age. In addition to the nature of samples and the analytical methods, we have examined the methods for calculating Ce anomalies. Based on these examinations, we have established a set of criteria to screen the data and accepted only the reliable data for further interpretation. In estimating the true and original REE characteristics of chemical precipitates in BIFs, we recommend the use of REE data that were obtained by the ICP-MS and/or the ID-TIMS methods on chemically pure BIFs samples. The samples must be essentially free of clastic components (i.e., $Al_2O_3 < 0.1$ wt%) and least-altered by syn- and post-depositional processes (i.e., preservation of fine-banding textures; absence of alteration minerals). To evaluate a true Ce anomaly, we recommend the combined use of the Ce_N/Ce_N^* and La_N/La_N^* ratios in which the Ce_N^* and La_N^* values are calculated by the back-extrapolation method using Pr, Nd, and Sm values. Normalization of the REE values against chondrite, rather than shale standards (e.g., PAAS and NASC), is a better method for identification of a true Eu anomaly in BIFs.

Applying the above approaches to the published data, we have recognized that most of the previously suggested negative Ce anomalies are artifact of positive La anomalies. Most BIFs show no Ce anomaly, but some younger BIFs show negative Ce anomalies. We have also recognized that a positive Eu anomaly is not a norm for BIFs. More than 50% of the BIFs, regardless of their ages, show either no or negative Eu anomaly. Based on the REE characteristics, BIFs may be divided into two major types: (1) those with positive Eu anomalies and no Ce anomaly; (2) those with no or negative Eu anomaly and negative Ce anomalies. Type 1 BIFs occur mainly in Archean, while type 2 BIFs occur mainly in Proterozoic. Transition from type 1 to 2 may have been caused by decreasing influence of high temperature hydrothermal fluids and increasing contribution of local seawater in the BIFs-forming environments. More high-quality analyses of REEs in BIFs of various ages and sedimentary environments are required for the development of the model for the BIFs deposition and for the chemical evolution of atmosphere and hydrosphere.

Klein C & Beukes NJ, *The Proterozoic Biosphere. A Multidisciplinary Study, Princeton University Press*, 139-146, (1992).