

## Concentration of Elements Related to Redox Evolution in Oceanic Environments

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Chemical sedimentary rocks, which are precipitates from ancient seawater, not only concentrate useful elements (e.g., Fe, Mn, Co, Ni, Rare Earth Elements (REEs)), but may also reflect changes in Earth's surface environments (e.g., pH, redox conditions, surface temperature). The temporal distribution of Banded Iron Formations (BIFs), the main economic Fe source, has been proposed to indicate changes in atmospheric and ocean chemistry in early Earth related to the evolution of the biosphere. However, to acquire a better understanding of the surface environments, BIFs deposited in various sedimentary setting need to be investigated. In this study, geological and geochemical investigations of BIFs that were deposited in a shallow ocean in the Archean Barberton Greenstone Belt, South Africa, show that the Cr/Ti and U/Th ratios are higher in the BIFs compared with the underlying and overlying clastic sedimentary rocks. Oxygen isotope compositions in each chromite grain, a host mineral of Cr, were determined by SIMS. The results show the chromite has lower  $\delta^{18}\text{O}$  values compared with igneous and metamorphosed chromites, indicating that they were formed under hydrothermal conditions. The results suggest that dissolved Cr and U species in ocean were coprecipitated with ferric (hydr)oxides during the formation of the BIFs, and that chromite was formed by later hydrothermal alteration. Therefore, the results of the study indicate that enrichments of redox-sensitive elements (e.g., Cr, U) in BIFs have already occurred through chemical processes as early as 3.2 billion years ago due to the oxygenation of a shallow part of the ocean.

Volcanogenic Massive Sulfide (VMS) deposits such as Kuroko deposits in the Hokuroku district, Akita Prefecture were formed by ancient submarine hydrothermal activity, and are also associated with Fe-rich chemical sedimentary rocks. Because VMS deposits are primarily composed of sulfide minerals that are unstable in an oxic environment, such as pyrite and chalcopyrite, an anoxic environment in the Hokuroku basin may play an important role in the preservation of sulfide ores. Therefore, REE patterns and Fe isotope compositions of the Fe-rich chemical sedimentary rocks were investigated since geochemical evidence of such an environment being present in the Hokuroku basin is currently lacking. The results of these analyses show that the  $\delta^{56}\text{Fe}$  values of samples occurring directly on and above Kuroko deposits were -1.5 to 0.5 ‰. These values are largely fractionated from the  $\delta^{56}\text{Fe}$  value of the standard (i.e., 0 ‰), which is similar to that of igneous rocks. The samples that have a large negative value also bears negative Ce anomaly. These signatures indicate that partial oxidation of dissolved ferrous iron occurred by mixing ferrous iron-bearing anoxic water with oxygen-bearing seawater, and therefore that the seafloor of the Hokuroku Basin was anoxic. On the other hand,  $\delta^{56}\text{Fe}$  values of chemical sedimentary rocks formed 2 - 3 Ma after the Kuroko deposits formed ranges from -0.8 to -0.3 ‰. These values are similar to those of dissolved ferrous ion in a modern seafloor hydrothermal fluid. Therefore, the  $\delta^{56}\text{Fe}$  values of the samples indicate near complete oxidation of dissolved ferrous iron in an oxic environment. Therefore, these results suggest that the depositional environment in the Hokuroku basin shifted from anoxic to oxic after the formation of Kuroko deposits.

Keywords: Chemical sedimentary rock, Banded Iron Formation, Barberton Greenstone Belt, Chromium, Volcanogenic Massive Sulfide deposit, Iron isotope