

Low $\delta^{57}\text{Fe}$ values record the onset of Palaeoproterozoic bacterial manganese reduction

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Iron and manganese share similar biogeochemical properties in modern near-surface environments, whereas Archaean and Palaeoproterozoic banded iron formations (BIF) are generally devoid of Mn. We present an Fe-isotope study of the transition from BIF to Mn-rich deposition in the Hotazel Formation, a unique inter-layered sequence of BIF and Mn-rich sediment in the uppermost part of the Palaeoproterozoic (2.7-2.4 Ga) Transvaal Supergroup of South Africa. Virtually unmetamorphosed and unaltered portions of the Hotazel sequence consist of chert-magnetite-ankerite-calcite-Fe silicate BIF that is cyclically intercalated with three manganiferous lutite layers dominated by Mn carbonate-braunite-hematite. The host BIF has an average bulk $\delta^{57}\text{Fe}$ (IRMM) of $-1.70 \pm 0.80\%$, and in areas where low-temperature hydrothermal carbonate leaching and oxidation are evident, it gives a comparable range of $\delta^{57}\text{Fe}$ values ($-1.98 \pm 0.58\%$). Lithological units transitional to the manganese layers ('hematite lutites'), as well as the Mn lutites themselves, give low $\delta^{57}\text{Fe}$ values of $-3.00 \pm 0.31\%$. These are the lowest $\delta^{57}\text{Fe}$ values recorded in early Precambrian hematite-rich sedimentary rocks. $\delta^{57}\text{Fe}$ values of the BIF are lower than magnetite-siderite-bearing BIF of the older Kuruman and Griquatown Formations of the Transvaal Supergroup [1].

Following Johnson *et al.* [1], we interpret the $\delta^{57}\text{Fe}$ data for the Hotazel BIF to reflect fractionation effects driven by dissimilatory bacterial Fe reduction (DIR) in an isotopically evolved Fe(II) reservoir. The presence of low $\delta^{57}\text{Fe}$ hematite in the Mn-rich layers, in conjunction with the co-abundance of low $\delta^{13}\text{C}$, Fe-poor manganiferous carbonates ($\delta^{13}\text{C}$ (PDB): -12.5 to -8% [2]) suggests that during intervals of increased Mn precipitation, DIR was curtailed in favour of bacterial Mn reduction for the first time on that scale in Earth's history. The hematite in these sediments would chemically represent the original Fe(III) precipitate and its isotope composition would approximate that of the dissolved Fe(II) pool, assuming that no fractionation effects accompanied aqueous Fe(II) oxidation.

[1] Johnson *et al.* (2008) *GCA* **72**, 151-169. [2] Tsikos *et al.* (2003) *Econ. Geol.* **98**, 1449-1462.

Geochemical mapping in Kobe area, southwest Japan: Elemental behaviors and controlling factors

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Environmental assessment of the Kobe area, Kinki district, southwest Japan has been made using geochemical mapping of stream sediments. The area consists mainly of the Cretaceous granitoids; Cretaceous volcanic clasts of the Arima Group; sandstone, mudstone, chert, limestone and basalts of the Jurassic accretionary complex of the Tamba belt; sandstone, conglomerate, mudstone and tuffs of the Miocene Kobe Group; and Pliocene to Pleistocene sand, gravel and clays of the Osaka Group. Some of the closed silver and copper mines are in the southeastern part of the study area.

Stream sediments were collected using an 80-mesh (180 μm) sieve in wet condition at each sampling site after the method of Tanaka *et al.* [1]. A total of 322 stream sediments over an approximately 2000 km^2 in the Kobe area were analyzed for 25 elements including Al, As, Ba, Ca, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Nb, Ni, P, Pb, Rb, Si, Sr, Th, Ti, V, Y, Zn, Zr with X-ray fluorescence spectrometry (XRF) and loss-on-ignition. Distributions of the major elements including Si, K, Na, Ca, Mg, Ti, Fe, Mn, Al, P are controlled by the chemical composition of the country rocks. The concentration of Zr is high (270 ppm ~ 4930 ppm) in sediments of the Sanda basin area because of the zircon sedimentation. Heavy metals including As, Cu, Ni, Pb, Zn give higher concentration spots in downstream regions of the closed mines.

Combining these geochemical map analyses and surface geology, the distribution patterns of the elements are mainly controlled by three factors: i) wide-areal regional elemental distribution powered by surface geology, ii) local distribution affected by sedimentation of the heavy minerals in the basin, and iii) spot deposition of ore minerals nearby the local mines.

[1] Tanaka *et al.* (1994) *J. Earth Planet. Sci. Nagoya Univ.* **41**, 1-31.