Marine redox evolution and Co-Mn signals of the Great Oxidation Event

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Oceanic ferromanganese nodules and crusts contain wt% levels of Co by virtue of adsorption of ionic Co(II,III) species onto Fe(III) and Mn(III,IV) oxyhydroxides under oxic marine conditions. Oxidation of Co(II) to Co(III) occurs under Eh-pH conditions broadly similar to those for Mn(II) oxidation to Mn(III,IV). Fe(II), by contrast, oxidizes to Fe(III) at lower redox potential under modern marine pH levels.

Neoarchean-Paleoproterozoic Iron Formations (IF) are generally impoverished in Mn (<0.50 wt% on average). Similarly, the global average of Co in the same IFs is only 2.0±2.7 ppm (Swanner et al., 2014). We have studied the Kuruman and Griquatown IFs and the younger Mn-hosting Hotazel IF of the 2.6-2.4 Ga Transvaal Supergroup in South Africa, in order to explore the temporal marine redox evolution of Mn and Co as potential proxies for global ocean chemistry leading up to the Great Oxidation Event (GOE). The Kuruman-Griquatown succession contains only occasional wt% contents of Mn in its uppermost part, hosted exclusively in carbonate phases. Bulk-rock Co concentration averages at 1.9±1.9 ppm, and speciation results show no obvious affinity to the Fe-oxide (magnetite) fraction. The Hotazel IF layers contain comparably low Mn (0.53±0.35 wt%) and Co (2.4±1.6 ppm) contents to the Kuruman-Griquatown IFs. However, bulk Co contents rise sharply to >100 ppm within the hematite-rich transitions to the interbedded Mn-rich layers. Within zones of maximum Mn concentration, Co abundances decline but remain between 10-50 ppm. Speciation results suggest a strong correlation between Co and the Fe(III) fraction (as hematite) of the rocks.

We interpret these signals as evidence for no Co and Mn oxidation for pre-GOE times during IF deposition, and thus no uptake of Co into either Fe(III) or Mn(III,IV) mineral species. During deposition of the Hotazel strata at the dawn of the GOE, however, oxidation of Mn and Co resulted in both species becoming active electron acceptors for the first time in the oceanic water column, with Co(III) sequestered almost entirely in the hematite mineral fraction.

Swanner *et al* (2014). *EPSL* **390**, 253–263.