



Sedimentary cobalt concentrations track marine redox evolution

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Oxygen production by photosynthesis drove the redox evolution of the atmosphere and ocean. Primary productivity by oxygenic photosynthesizers in the modern surface ocean is limited by trace nutrients such as iron, but previous studies have also observed high Co uptake associated with natural cyanobacterial populations. Constraining the size and variation of the oceanic reservoir of Co through time will help to understand the regulation of primary productivity and hence oxygenation through time. In this study, Co concentrations from iron formations (IF), shales and marine pyrites deposited over nearly 4 billion years of Earth's history are utilized to reconstruct secular changes in the mechanisms of Co removal from the oceanic reservoir. The Co reservoir prior to ~2 Ga was dominated by hydrothermal inputs and Fe(III)oxyhydroxides were likely involved in the removal of Co from the water column. Fe(II) oxidation in the water column resulted in the deposition of IF in the Archean and Paleoproterozoic, and the Co inventory of IF records a large oceanic reservoir of Co during this time. Lower Co concentrations in sediments during the Middle Proterozoic signify a decrease in the oceanic reservoir due to the expansion euxinic environments, corresponding to the results of previous studies. A transition to an oxidized deep ocean in the Phanerozoic is evidenced by correlation between Co and manganese (Mn) concentrations in hydrothermal and exhalative deposits, and in marine pyrites. This relationship between Co and Mn, signifying deposition of Co in association with Mn(IV)oxides, does not occur in the Precambrian. Mn(II) oxidation occurs at higher redox potentials than that required for Fe(II) oxidation, and the extent of Mn redox cycling prior to full ventilation of the oceans at the end of the Neoproterozoic was likely limited to spatially restricted oxic surface waters. In this regard, Co is another valuable redox proxy for tracking the growth and decline in oxygenated settings, complementary to other metals that are characteristically enriched under euxinic conditions (i.e. Mo, Zn and Cu) and anoxic (i.e. U, Re and Os) conditions, even as the availability of Co may have influenced primary productivity.