Ni isotope anomaly in banded iron formations prior to the Great Oxidation Event

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Konhauser et al. proposed that the Great Oxidation Event (~2.4 Ga) may have been triggered and/or sustained, at least in part, by a reduction in methanogen productivity in the Late Archean Eon. The methanogen decline would in turn have been caused by sharply reduced availability of dissolved Ni, which is an essential nutrient for methanogens, in Archean oceans [1,2]. This “Ni famine” hypothesis followed the observation of relatively high maximum Ni/Fe ratios in Archean banded iron formations (BIF), a sharp decline in Ni/Fe ratios between 2.7 and 2.4 Ga, and lower Ni/Fe ratios ever since. Because methanogens are known to strongly fractionate the stable isotopes of Ni [3], we are working to test the “Ni famine” hypothesis by looking for a shift in Ni isotope compositions in BIF over time that might reflect a Late Archean Eon change in methanogen Ni status and might coincide with the observed decline in Ni concentrations.

Our preliminary results indicate that the ocean’s Ni isotopic composition has varied considerably over geologic time and also point to a likely first-order disturbance to the biogeochemical cycle of Ni between 2.7 and 2.4 Ga. We have analyzed bulk samples from BIF for which Cr isotopes were previously published [4]. We find that nearly all the samples are significantly lighter in terms of $\delta^{60/58}Ni_{SRM986}$ than modern seawater, which has $\delta^{60/58}Ni_{SRM986}$ = 1.4 ‰ [5]. How Ni isotopes fractionated during incorporation into BIF from Precambrian seawater is unknown, as are effects of diagenesis, but, using experimental results from [6], average $\delta^{60/58}Ni_{SRM986}$ for Precambrian seawater can be roughly estimated from our results as ~0.9 - 1.0 ‰ Additionally, we observe the very heaviest and very lightest Ni isotope compositions in those BIF samples aged 2.7-2.4 Ga, indicating significant changes in the controls on $\delta^{60/58}Ni_{SRM986}$ in these samples relative to the rest of the Precambrian.

[1] Konhauser et al. (2009) *Nature* 458,750; [2] Konhauser et al. (2015) *Astrobiology* 15,804; [3] Cameron et al. (2009) *PNAS* 106,10944; [4] Frei et al. (2009) *Nature* 461, 250; [5] Cameron and Vance (2014) *GCA* 128,195; [6] Wasylenki et al. (2015) *ChemGeol* 400,56.