Ni Isotopes in the Archaean Mount McRae Black Shale

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The ~2.5 Ga Mt. McRae Shale records excursions in a number of geochemical signals that have been interpreted to represent an early pulse of oxygenation at Earth's surface [1, 2]. Of particular interest are very light $\delta^{13}C$ values in organic carbon [1], which could have been produced by methanotrophs. Nickel is an essential micronutrient to methanogens/trophs, and these organsisms have also been shown to fractionate Ni isotopes [3]. We are targeting Ni concentrations and stable isotopes in black shale samples from ~110-190 m depth in the Mt. McRae core ABDP-9 [1,2] to see if we can detect a signature of methanogenesis/trophy. Like some other metals, the concentrations of Ni in the shales spike during the interval from ~125-153 m (referred to as S1), which is thought to record the pulse of oxygen, followed by a return to anoxic conditions [1,2]. Because Ni is critical to methanogens/trophs, Ni isotopes might offer new insight into the role of these biological processes in the Archaean.

Here we present preliminary Ni stable isotope compositions of twenty samples of the Mt. McRae Shale [1,2]. The samples have a wide range of $\delta^{60}Ni$ from +0.2 to +1.4‰. The Ni isotope compositions of samples from within the S1 interval are slightly heavier and more variable than samples from other parts of the sequence. The average $\delta^{60}Ni$ of ten S1 samples is 0.78 ± 0.29‰, while the average for ten samples from before and after S1 is 0.40 ± 0.15‰ (1SD). The overall heavier Ni isotopes in the S1 section likely reflect the delivery of heavier dissolved Ni to the oceans over that time due the retention of lighter Ni by Fe-oxides during oxidative rock weathering [4]. The greater variability of Ni isotopes in S1 is due to large shifts in $\delta^{60}Ni$ (+0.3 to +1.4‰) of samples in the short interval from ~135-137 m. This interval also records an excursion to very light $\delta^{13}C$ in organic carbon [1]. It is possible that the highly variable Ni isotope compositions at that time reflect instability in the marine Ni cycle caused by an increase in the importance of methanotrophy and methanogenesis in the biogeochemical cycle of Ni.

[1] Kaufman *et al* (2007) *Science* **317**, 1900; [2] Anbar *et al* (2007) *Science* **317**, 1903; [3] Cameron *et al* (2009) *PNAS* **106**, 10944; [4] Spivak-Birndorf *et al* (2013) 125th *GSA meeting*, abst. #149-7