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Nitrogen cycling in the late Paleoproterozoic freshwater environment

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The Paleoproterozoic (2.5–1.6 Ga) was a key period in Earth's environmental and biological evolution, because the atmospheric oxygen level was raised during the *ca.* 2.4 Ga Great Oxidation Event (GOE) and *ca.* 2.2 Ga Lomagundi-Jatuli Event [1]. It is generally accepted that surface ocean was pervasively oxygenated after the GOE [1]. Recent studies suggest aerobic nitrogen cycles in the Paleoproterozoic ocean based on positive nitrogen isotope compositions (~+5 ‰) [2, 3]. However, the nature of nitrogen cycling in freshwater environments is still obscure. Here, we present redox-sensitive element and nitrogen isotope compositions of black shales in the 1.84 Ga Embury Lake Formation, Flin Flon belt, Canada.

The Embury Lake Formation consists of turbiditic sandstone-black shale alterations. Black shales from the formation are characterized by low total sulfur (TS) and total organic carbon (TOC) contents. The average TS/TOC value of the black shales is 0.05, which is comparable to the values reported for modern freshwater sediments [4]. Therefore, it is inferred that the turbiditic sequence have been formed in a sulfate-poor basin, such as lacustrine [4].

Manganese is poor in the black shales, suggesting deposition under suboxic to anoxic conditions. Redox sensitive elements (V, U, and Cr) exhibit positive correlations with detrital tracers, Al and Ti. Since the three redox sensitive elements are authigenically accumulated to sediments under anoxic conditions [5], the positive correlations indicate suboxic conditions during deposition of the Embury Lake Formation. $\delta^{15}N$ values of the black shales are mostly less than <+1‰, suggesting nitrate poor environment. The $\delta^{15}N$ values are distinct from that of the previously reported coeval ocean sediments [2, 3]. It is expected that nitrate has been exhausted by denitrifier in freshwater environment while available for nitrate assimilation organisms in the ocean.

[1] Lyons et al. (2014), *Nature* **506**, 307-315. [2] Kipp et al. (2018), *EPSL.* **500**, 117-126. [3] Godfrey et al. (2013), *Geology* **41**, 655-658. [4] Motomura et al. (2020), *Island Arc* **29**, e12343. [5] Algeo & Maynard (2004), *Chem. Geol.* **206**, 289-318.