

Migrations of sediment redox boundaries as indicators of change in oligotrophic systems

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In oligotrophic environments, such as the deep Arctic Ocean, the depth of oxygen penetration (OPD) into sediments is deep and highly sensitive to the supplies of oxygen and organic matter from the overlying water [1]. Recorded in the distribution of redox-sensitive metals, changes in the OPD may reveal temporal trends in trophic conditions. In sediments recovered from the deep basins of Lake Superior, oxygen penetrated below diagenetic layers of iron and manganese by 3 cm or more in both June and October. This suggests either a long-term decrease in the productivity of the lake or large seasonal changes. The latter may result from changes in the bottom water oxygen levels, which fluctuate by about 10%. These large OPD migrations would strongly affect sediment effluxes of nutrients, such as nitrate. Herein we discuss challenges in detecting the temporal variations in sediment redox balance, in determining their time scale and time lags, and accounting for the effects of strong lateral heterogeneity in sediment properties. Based on our diagenetic studies, we place new constraints on nutrient budgets in Lake Superior.

[1] Katsev *et al.* (2006) *Limnol. Oceanogr.* **51**, 1581–1593.

Nitrogen in the Canadian Shield: Resolving abiotic contributions and biological cycling

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There is increasing interest in understanding the Earth's geological nitrogen budget and reservoirs - a topic important not only for understanding greenhouse warming on the early Earth [1], but for understanding the environment in which life arose. While hydrocarbon gases and H₂ have been investigated in the > 2 Ga rocks of the Canadian Shield - to date little research has been undertaken on the substantial quantities of molecular nitrogen (N₂) also found in these subsurface environments.

The results of gas content (by gas chromatography) and nitrogen isotope (by GC-IRMS) analyses show a clear positive relationship between N₂/O₂ and δ¹⁵N_{N₂} for samples with N₂/O₂ < 20, indicating the low δ¹⁵N_{N₂} values are attributable to air contamination. However, samples with N₂/O₂ > 20 show a narrow range of 7-9‰ in δ¹⁵N_{N₂}, with a few samples as enriched as +17.5‰. The δ¹⁵N_{N₂} values seem to be quite uniform compared to the hydrocarbon and H₂ gas geochemistry and isotopic signatures - which have been shown to vary significantly from one site to another based on the relative dominance of microbial processes, versus abiotic water-rock reactions, such as H₂-producing radiolysis and/or serpentinization coupled to hydrocarbon formation via Fischer-Tropsch synthesis and polymerization.

The kinetic isotope effect associated with thermal decomposition of NH₃ is large (17‰). Generally, denitrification and ammonia oxidation are also associated with large kinetic fractionation effects (>10‰) with only a few small fractionation effects (<3‰) observed for microbial denitrification. The δ¹⁵N_{N₂} values may be relatively constant if equilibrium isotope fractionation between N₂ and its source species can be reached, although equilibration is unlikely at temperatures <300°C. Ongoing investigation of δ¹⁵N of ammonium and nitrate in the hosting saline ground waters and rocks will help to further evaluate the sources and sinks of N₂ in this setting.

[1] Goldblatt *et al.* (2009) *Nature Geoscience* **2**, 891–896.