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# NITROGEN CYCLING IN THE LATE PALEOPROTEROZOIC REDOX STRATIFIED OCEAN

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## ABSTRACT

Nitrogen cycling has been evaluated across a depth transect in the late Paleoproterozoic Animikie Basin, spanning the end of Earth's final period of global iron precipitation and a major transition to euxinic conditions in areas of high productivity. Sediments from near shore where productivity was highest have $\delta^{15}N$ compositions up to ~3‰ higher than at more distal sites. This suggests that as $NH_4^+$ mixed vertically upwards into the photic zone, it was either assimilated by organisms or oxidized. Subsequent enhanced production of $N_2$ by denitrification or anammox led to the observed increase in $\delta^{15}N$ close to shore. Any deficit in biologically available N was overcome by $N_2$-fixing organisms, but the input of N with low $\delta^{15}N$ from this process did not overwhelm the increase in $\delta^{15}N$ from denitrification. Since there is no evidence for conditions of severe N-stress arising from trace metal limitation (particularly Mo) of N fixation during the transition to euxinic conditions, losses of N were either very small (potentially because low $O_2$ levels limited $NH_4^+$ oxidation), or alternative pathways which retained N were important. The fact that Mo appears to have remained bioavailable for N fixation, either suggests that the extent or severity of sulfidic water column conditions was not sufficient to quantitatively sequester Mo on a global scale, or that rivers directly delivered Mo to surface waters on the inner shelf. The effects of $N_2$ fixation on $\delta^{15}N$ increased to more distal parts of the shelf, consistent with models invoked for modern upwelling zones over broad continental margins.

## INTRODUCTION AND SETTING

Around 1840 Myr ago, a widespread transition to euxinia occurred along productive continental margins (Canfield, 1998; Poulton et al., 2004; 2010; Kendall et al., 2011). These anoxic sulfidic conditions extended outwards from near shore to the mid-shelf, and were overlain by oxic surface waters, with deeper waters that were anoxic and Fe-rich (ferruginous) (Poulton et al., 2010; Kendall et al., 2011; Planavsky et al., 2011). Widespread sulfidic conditions throughout the mid-Proterozoic have been implicated in the protracted oxygenation of the atmosphere and slow rates of eukaryotic evolution (Anbar and Knoll, 2002). However, the continuation of ferruginous deep water conditions through the Mesoproterozoic, with sulfidic conditions limited to areas of high organic C production (Scott et al., 2008; Kendall et al., 2009, 2001; Poulton et al., 2010; Poulton and Canfield, 2011; Planavsky et al., 2011), highlights that the controls on productivity, and oxygenic productivity in particular, remain poorly understood.

One major question concerns feedbacks associated with the N cycle, and is the focus of this study. The classical view of the N cycle is that as anoxic, $NH_4^+$ bearing deep water vertically mixed into oxic surface water, nitrification-denitrification and anammox reactions would have severely depleted the ocean inventory of dissolved fixed N (Fennel et al., 2005). Furthermore, it has also been suggested that expansive euxinia may have placed additional stress on the N cycle by the precipitation of chalcophiles such as Mo and Fe, which are essential to $N_2$ fixation (Anbar and Knoll, 2002). However, the ocean inventory of these metals had to become extremely depleted in order to restrict N-fixation (e.g., Zerkle et al., 2006). Recent evidence for the persistence of ferruginous deep ocean conditions through the mid-Proterozoic (Poulton et al., 2010; Planavsky et al., 2011), coupled with the likelihood that Fe was present in solution even under euxinic conditions (potentially as $FeS_{(aq)}$ clusters; Luther et al., 1996), suggests that Fe was unlikely to be biolimiting at this time. In terms of Mo, estimates based on $\delta^{98}$Mo suggest that the extent of sulfidic water column conditions may have been an order of magnitude higher than at present (Kendall et al., 2011), which may not have been sufficiently depleted to restrict $N_2$ fixation on a global scale. Furthermore, while sediment Mo and reactive Fe measurements address overlying water, they do not account for the whole of water column, including the upper ocean where the N cycle is most active. Consequently a direct evaluation of the operation of the N cycle is needed to determine its state during this major transition in ocean chemistry.

We report new N and C isotope data for sediments from six drill cores that provide a 350 km long oblique transect to the paleo-coastline of the Animikie Basin on the margin of Superior Province (Figure 1; Poulton et al., 2010). The Gunflint and Biwabik iron formations, which accumulated in a back-arc basin setting 1878±1.3 Myr ago (Fralick et al., 2002), are overlain by ejecta material from the Sudbury impact event, deposited sub-aerially during regression of the ocean at ~1850±1 Myr ago (Krogh et al., 1984). Later flooding from the south led to deposition of fine grained siliciclastic material of the Rove and Virginia Formations ~1836±5 Myr ago (Addison et al., 2005). The lower 100 m of these formations is dominated by black shales, with turbidites, derived from the north, gaining importance above this zone. Estimated water depths are between ~100 to 400 m, with good connectivity to the world ocean (Rasmussen et al., 2012). Iron speciation measurements suggest that a transition to persistently sulfidic mid-depth water in near shore environments occurred in the Rove and Virginia Formations, while deeper waters remained ferruginous (Poulton et al., 2010), providing an ideal setting in which to study the N cycle during this important transition in ocean chemistry.

## RESULTS AND DISCUSSION

Analytical methods, data and discussion about the preservation of primary $\delta^{15}N$ can be found in the on-line supplement.

### Spatial variations in organic carbon and $\delta^{13}C_{org}$ across the Animikie Basin shelf

Concentrations of $C_{org}$ are similar across the shelf during iron formation deposition, only increasing in a few thin tuffaceous layers. In the siliciclastic Rove and Virginia Formations there is a tripling in $C_{org}$ concentration towards the shore. If sediment accumulation rates were higher near shore than at the distal sites, as is typical, and indicated by the up-core increase in grain size in cores MC-1 and PR9-1, the $C_{org}$ distribution is consistent with an increase in $C_{org}$ accumulation due to higher productivity associated with mixing through coastal upwelling. The development of sulfidic water overlying deeper ferruginous water is analogous to modern oxygen minimum zones associated with upwelling and high OM fluxes, but because of limited $O_2$ and $NO_3^-$, $SO_4^{2-}$ was respired at a rate higher than that at which deeper water Fe(II) was supplied (Poulton et al., 2010; Planavsky et al., 2011). Organic $\delta^{13}C$ varies between -27 and -34‰ in both iron formation and siliciclastic sediments (Figs 1B and 2), typical of values for Proterozoic sediments (Karhu and Holland, 1996; Kaufman et al., 1997; Bekker and Kaufman. 2007). While $\delta^{13}C_{org}$ is evenly distributed across the Gunflint-Biwabik shelf, there is a trend of decreasing $\delta^{13}C_{org}$ shoreward in association with increasing $C_{org}$ during deposition of the Rove-Virginia Formations (Fig. 1). Lower $\delta^{13}C_{org}$ and higher $C_{org}$ suggests that $CH_4$ fluxes resulting from high productivity near shore were oxidized aerobically or anaerobically with $SO_4^{2-}$.

## Spatial variations in $\delta^{15}N$ and a nitrogen isotope model for the Animikie Basin

Unlike C, N is a limiting nutrient and when productivity consumes all available $NO_3^-$, $NH_4^+$ or $NO_2^-$ (cumulatively dissolved inorganic N; DIN), $\delta^{15}N_{OM}$ will be similar to the isotope composition of DIN available at a particular location. $\delta^{15}N_{OM}$ can be lower than $\delta^{15}N_{DIN}$ if there are other limitations on production and DIN is not fully consumed, or if there are diazotrophs present. Except for $N_2$-fixation and ammonification of OM, each transfer step of N between different phases is accompanied by strong isotope discrimination which favors the light isotope in all but one step, $NO_2^-$ oxidation (Casciotti, 2009, and references therein). The N cycle is sensitive to the availability of $O_2$ and, when the N and O cycles interact, the isotope composition of DIN as well as its N inventory can be influenced. Organic matter sinking from the surface ocean decays and forms $NH_4^+$. In an anoxic ocean, $NH_4^+$ is returned to the surface ocean where it is consumed, while in a fully oxic ocean, nitrifying bacteria immediately oxidize this $NH_4^+$ to $NO_3^-$, and $NO_3^-$ is returned to the surface ocean. Where redox gradients exist, either due to a weakly oxygenated atmosphere or because $O_2$ is drawn down by respiration, there is potential for substantial losses of N by autotrophic anammox or classical denitrification, which will increase $\delta^{15}N_{DIN}$. However, the geological $\delta^{15}N$ record, $\delta^{15}N_{SED}$, is derived from export production, and reflects the biological response to N availability, and thus will be affected by $N_2$-fixation responding to DIN deficits (Deutsch et al., 2004).

During the deposition of the iron formation, $\delta^{15}N$ deposited on the outer shelf was about 1‰ lower than on the inner shelf, excluding tuffaceous layers which have variable $\delta^{15}N$ values. After euxinic conditions developed on the inner shelf, sediment $\delta^{15}N$ at the inner shelf sites remained at ~5.3‰ with outer shelf sites ~1.4‰ lower. A one-way ANOVA was used to confirm that $\delta^{15}N_{SED}$ differed between the inner and outer shelf, $F(4, 174) = 39.6$, $p < .001$. While changes in the distribution of $C_{org}$ concentrations and $\delta^{13}C_{org}$ across the shelf reflect enhanced coastal mixing and productivity, the distribution of $\delta^{15}N_{SED}$ across the shelf was largely unchanged, suggesting little change in the operation of the N cycle during a time when profound changes in ocean chemistry took place.

Ammonium would have been the stable form of N in ferruginous and euxinic water, with $NO_3^-$ stable in oxic surface water. The base of the mixed layer would have coincided with the redox gradient between oxic surface water and either ferruginous deep water or euxinic mid-depth water. $NH_4^+$ mixing upwards was either biologically assimilated or oxidized to $NO_2^-$ or $NO_3^-$, the process of nitrification. The oxidized forms of DIN could have been assimilated or reduced to $N_2$ in order to respire $C_{org}$ or oxidize reduced metal or S species (Fig. 2 node A). Which of these processes dominated the $NH_4^+$ flux was probably determined by upwelling rates, surface water $O_2$ concentration and the organisms that were present, but the potential for DIN losses were large.

If N and associated metal co-factors were the main controls on productivity, for productivity to be highest on the inner shelf, either the activity of anoxygenic phototrophs kept $O_2$ levels low (which limited nitrification; Johnston et al, 2009), organisms were actively fixing N, or there were mechanisms which circumvented denitrification and anammox. Nitrification, denitrification and DIN assimilation select for $^{14}N$. In a redox layered ocean, oxidation and assimilation of upwelling $NH_4^+$ both occur at the chemocline and may consume all $NH_4^+$ entering the euphotic zone. If nitrification and assimilation selected equally for $^{14}N$, biomass grown from $NH_4^+$ and $NO_2^-/NO_3^-$ would have had similar $\delta^{15}N$, and equal to the deep source of $NH_4^+$. If all the $NO_2^-/NO_3^-$ was then denitrified and lost to the atmosphere, there would be no net effect on $\delta^{15}N$ by denitrification and the deep $NH_4^+$ reservoir, biomass and sediment $\delta^{15}N$ would have been the same as $N_2$ fixed by diazotrophs, ~0‰. The very negative $\delta^{15}N_{SED}$ of the Mesozoic ocean anoxic events has been explained by large vertical fluxes of $NH_4^+$, also predicted to be the dominant N species at depth, which fueled productivity and due to its high concentration, exhibited greater isotope discrimination than nitrification (Higgins et al., 2012). The positive values of $\delta^{15}N_{SED}$ on the Animikie margin suggest that mixing did not lead to high $NH_4^+$ concentrations where it was assimilated which reduced the ability of assimilation to discriminate against $^{15}N$ (Hoch et al., 1994), or that subsequent reduction of $NO_2^-/NO_3^-$ was not quantitative. If $^{14}N$ was partitioned into $NO_2^-/NO_3^-$ because of low deep $NH_4^+$ concentrations, quantitative denitrification would have increased remaining DIN, requiring high rates of $N_2$-fixation to sustain productivity and moderate $\delta^{15}N_{SED}$. For N-fixation rates to be high, this implies that Mo could not have been limiting, either because euxiunic conditions were not severe enough or that Mo was supplied directly into the coastal system by nearby river systems (Maric and Fralick, 2005). However, the stability of $NH_4^+$ in ferruginous and sulfidic water suggests that deep $NH_4^+$ concentrations were unlikely to be particularly low, so in order for $\delta^{15}N_{SED}$ to be positive, denitrification could not have been quantitative. The fate of $NO_3^-$, either direct assimilation or conservation through dissimilatory nitrite reduction to ammonia (DNRA; or respiratory ammonification) or denitrification (Fig 2, node B) determined how 'leaky' the system was toward N, and how much N fixation was required to make up the deficit. While DNRA was once thought to be restricted to euxinic systems (Sørensen, 1978; Simon, 2002; Senga et al., 2006; Tugtas and Pavlostathis, 2007), its occurrence in the Benguela and Peru upwelling systems (Kartal et al., 2007; Lam et al., 2009) suggests that the presence of sulfide is not a pre-requisite, and it occurs over a range of $O_2$ concentrations (Kraft et al., 2011). The strong redox gradient suggests that N losses and $\delta^{15}N$ could have been high above euxinic areas of the margin. The inference from $C_{org}$ is that euxinic conditions did not limit productivity, and hence either DNRA was effective at retaining $^{14}N$-rich DIN in the coastal zone, or the high productivity was fueled by N-fixation.

The $\delta^{15}N$ distribution indicates that as surface water moved away from the coastline, it likely carried a N deficit (Fig. 2 inset). Assuming the lower $\delta^{15}N_{SED}$ at distal sites reflects increased diazotrophy, then as discussed above, the Fe(II)-bearing deep ocean was able to supply labile Fe to the surface ocean, while Mo was also not limiting, either due to non-quantitative removal under euxinic conditions and lateral mixing from the inner shelf, or by vertical mixing of ferruginous water in from which Mo had not been sequestered.

**Implications for the Proterozoic N cycle.**

It has been predicted that sulfidic conditions in the mid-Proterozoic redox-stratified water column would have led to severe N-limitation, due to N losses and sequestration of the chalcophilic metals (particularly Mo and Fe) used in cofactors of various enzymes employed in the N cycle, especially those related to N-fixation (Anbar and Knoll, 2002; Glass et al., 2009). The lack of change in $\delta^{15}N$ as free $HS^-$ appeared in the Animikie Basin, combined with the highest productivity coinciding with euxinic conditions, do not support this model of extreme N stress. Either euxinia was not severe enough to lower Mo concentrations to levels which affected N-fixation, or continental run-off delivered Mo directly to coastal systems. Furthermore, pathways retaining N such as DNRA, could have mitigated DIN loss and its associated isotope effect because the $^{14}N$-rich $NO_2^-$ was converted back to $NH_4^+$ and not lost to the atmosphere as $N_2$. Consideration of the N cycle in the geological past should include all potential pathways, especially those of great antiquity that developed under regimes of extreme N limitation very early in the development of N metabolism (Mancinelli and McKay, 1988; Klotz and Stein, 2008).

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## FIGURE CAPTIONS

Figure 1. Six cores from the margin of the Superior Province (A) constitute a transect of samples across the Animikie Basin margin (B) and consist of iron formation and siliciclastic material interspersed with occasional other lithologies(C). Ejecta from the Sudbury meteorite impact provide~~s~~ a correlative layer across the basin from shallow water at MC-1 to distal shelf at MGS8. Ferruginous versus euxinic conditions are from Poulton et al., (2010). $\delta^{13}C_{org}$ (D) and $\delta^{15}N$ (E) exhibit persistent gradients across the margin.

Figure 2. The N cycle in the Paleoproterozoic is strongly influenced by the redox gradient which separated oxygenated surface ocean from deep ferruginous water or euxinic mid- depth water which developed in productive near shore environments. Deep $NH_4^+$ upwells at the coast and crosses the redox boundary where it can be nitrified to $NO_2^-/NO_3^-$ or assimilated (node A), the pathway taken may be influenced by $O_2$ availability and upwelling rate. $NO_2^-/NO_3^-$ can be respired to $N_2$ or reduced directly to $NH_4^+$ by DNRA (node B). The proportion of $NO_2^-/NO_3^-$ which is converted to $N_2$ determines the loss of N from the coastal system and the enrichment in remaining dissolved fixed N in $^{15}N$ and DIN deficit. The inset diagram depicts changes in N/P and $\delta^{15}N$ as water flows through this system. The deficit in DIN may promote N-fixation which introduces N with low $\delta^{15}N$, but it cannot overcome the strong preference for $^{14}N$ shown by denitrification unless all upwelling $NH_4^+$ is lost. R is the Redfield ratio, although it may deviate from R according to the ocean average biological requirements.