



# Nitrogen isotope evidence for alkaline lakes on late Archean continents



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## ABSTRACT

Nitrogen isotope ratios in ancient sedimentary rocks are generally interpreted as a proxy for metabolic nitrogen pathways and the redox state of the water column. Fractionation processes occurring under anoxic, alkaline conditions during the dissociation of  $\text{NH}_4^+$  to  $\text{H}^+$  and volatile  $\text{NH}_3$  are frequently overlooked, although this mechanism imparts large isotopic fractionations. Here we propose that  $\text{NH}_3$  volatilization is largely responsible for  $\delta^{15}\text{N}$  values of up to +50‰ at high C/N ratios in the late Archean Tumbiana Formation. This sequence of sedimentary rocks represents a system of lakes that formed on subaerial flood basalts and were partly filled by basaltic volcanic ash. Aqueous alteration of volcanic glass followed by evaporative concentration of ions should have led to the development of high alkalinity with a pH of 9 or higher, as in modern analogues. In this sedimentologically unusual setting, nitrogen isotope ratios thus provide indirect evidence for the oldest alkaline lake system in the rock record. These very heavy lacustrine  $\delta^{15}\text{N}$  values contrast markedly with those of Archean marine sedimentary rocks, making a Precambrian “soda ocean” unlikely. Today, alkaline lakes are among the most productive ecosystems on Earth. Some nutrients, in particular molybdenum, are more soluble at high pH, and certain prebiotic reactions would likely have been favored under alkaline conditions in similar settings earlier in Earth's history. Hence alkaline lakes in the Archean could have been significant for the origin and early evolution of life.

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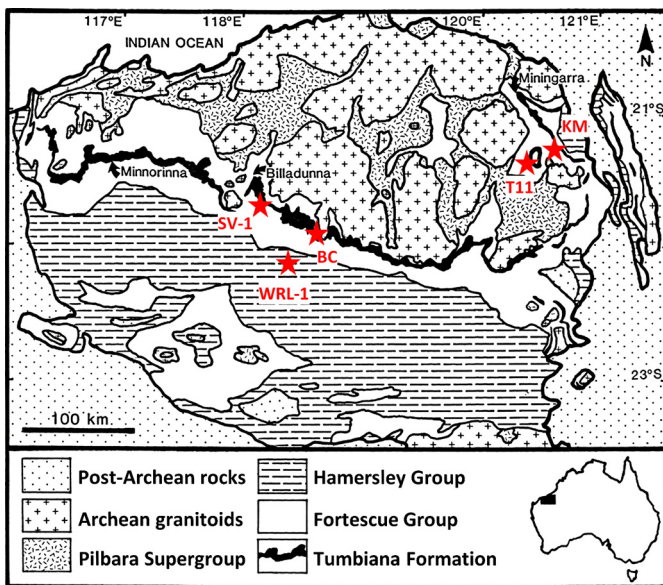
## 1. Introduction

Since ~2.7 Gyr, isotope fractionation in the marine nitrogen cycle has probably been dominated by redox reactions, in particular the large fractionation of up to 30‰ imparted during denitrification and/or anammox in the water column (Brunner et al., 2013; Garvin et al., 2009; Godfrey and Falkowski, 2009). In the modern ocean, these processes render residual  $\text{NO}_3^-$ , the major dissolved nitrogen species, isotopically enriched to ~+5‰, and this enrichment is passed on to biomass that incorporates  $\text{NO}_3^-$  as a nitrogen source (Sigman et al., 2009). In the early and mid-Archean, prior to the onset of oxidative weathering on land (Stüeken et al., 2012), the nitrogen cycle was evidently anaerobic, marine nitrate was scarce, and  $\text{N}_2$ -fixation was probably dominant leading to  $\delta^{15}\text{N}$  values near 0‰ (Beaumont and Robert, 1999), i.e. close to the composition of the atmosphere (Marty and Dauphas, 2003; Marty et al., 2013; Nishizawa et al., 2007). The time around 2.7 Gyr has been proposed as a transition from nitrate-depleted to nitrate-

rich conditions in surface environments (Thomazo et al., 2011). More specifically,  $\delta^{15}\text{N}$  values of up to +50.4‰ from the 2.72 Gyr lacustrine Tumbiana Formation in the Fortescue Group, Western Australia (Fig. 1), were interpreted as evidence of partial nitrification of  $\text{NH}_4^+$  under low ambient oxygen levels to isotopically light  $\text{NO}_2^-$  or  $\text{N}_2\text{O}$ , which were then lost from the system by either complete denitrification ( $\text{NO}_2^-$ ) or direct escape into the atmosphere ( $\text{N}_2\text{O}$ ) (Thomazo et al., 2011). The residual heavy  $\text{NH}_4^+$  would then have served as the major nitrogen source for living organisms such that its isotopic composition was preserved in the rock record. This process is not implausible, but it may not necessarily have been the major contributor to the observed fractionations in the Tumbiana Formation. First,  $\text{N}_2\text{O}$  is only a byproduct of nitrification with nearly 90% of initial  $\text{NH}_4^+$  going to  $\text{NO}_2^-$  (Stein et al., 2012). While some methanotrophic bacteria can fractionate nitrogen isotopes by up to 55‰ during the conversion of  $\text{NH}_4^+$  to  $\text{N}_2\text{O}$  (Mandernack et al., 2009), nitrification to  $\text{NO}_2^-$  usually imparts fractionations of up to 38‰ (reviewed by Casciotti, 2009). Therefore, a large fraction of  $\text{NH}_4^+$  would have to be oxidized to  $\text{NO}_2^-$  and subsequently lost from the system in order to explain  $\delta^{15}\text{N}$  values of up to +50‰. Assuming a starting composition of 0‰, over 72% would have to be lost, combined with Rayleigh fractionation. This

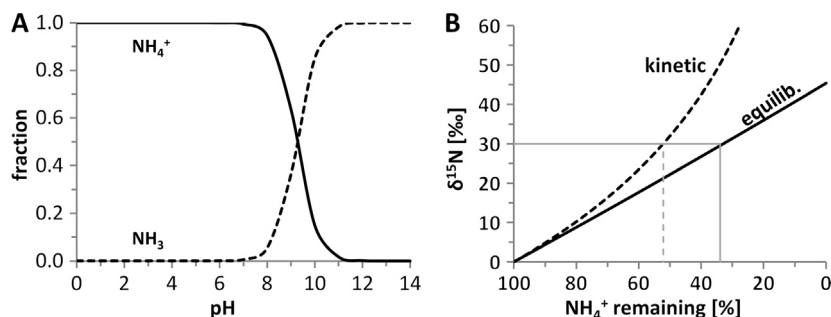
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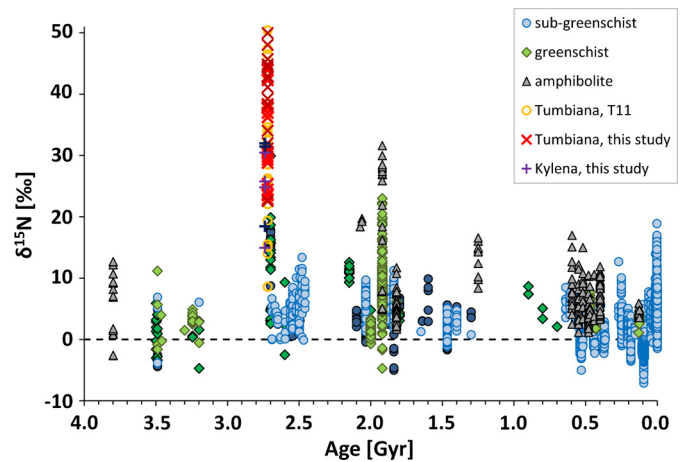


**Fig. 1.** Geographic sample locations in the Fortescue Group, Western Australia. SV-1, WRL-1 = locations of drill cores used in this study; T11 = location of the drill core studied by Thomazo et al. (2011); BC = outcrop locality in Beabea Creek; KM = outcrop locality of the Kylene Formation, Mopoke Member. Adapted from Buick (1992).

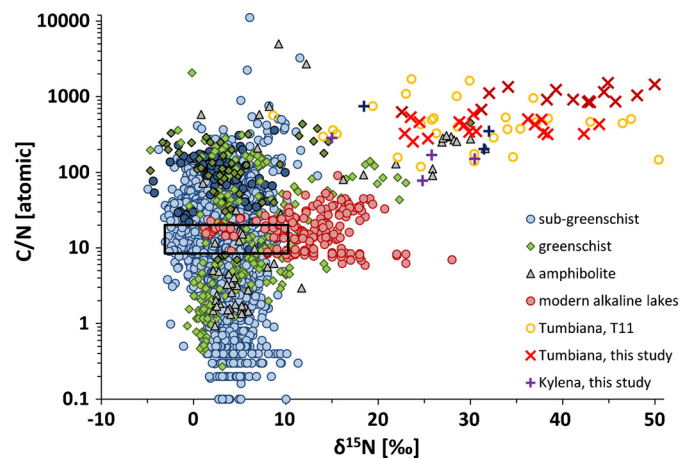
may be incompatible with the proposition (Thomazo et al., 2011) that the residual  $\text{NH}_4^+$  supply was still large enough to sustain the vigorous ecosystem recorded in the Tumbiana rocks. Indeed, the relationship noted between heavy  $\delta^{15}\text{N}_{\text{bulk}}$  values and high TOC levels (Thomazo et al., 2011) suggests that, if this mechanism were operating, then highest productivity occurred when  $\text{NH}_4^+$  would have been most limited. Second, as also noted by Farquhar et al. (2014), it is difficult to explain why little of the isotopically light  $\text{NO}_2^-$  would have been re-assimilated rather than denitrified, if  $\text{NH}_4^+$  had become limiting due to partial oxidation. Lastly, the Tumbiana Formation not only stands out because of its uniquely heavy isotopic composition (Fig. 2), but also because of its remarkably high  $\text{C}_{\text{org}}/\text{N}_{\text{bulk}}$  ratios ( $485 \pm 327$ , Fig. 3) (Thomazo et al., 2011, this study). This results from nitrogen concentrations that are unusually low (<21 ppm, this study), despite the moderately high total organic carbon (TOC) concentrations (up to 0.76%, this study) and the very low metamorphic grade (prehnite–pumpellyite, Smith et al., 1982) of these rocks. For these three reasons, we propose that an additional mechanism with a marked preference for  $^{14}\text{N}$  over  $^{15}\text{N}$  must have contributed to nitrogen loss from the water column and perhaps during diagenesis. Volatilization of  $\text{NH}_3$  under alkaline conditions would fulfill this condition and is consistent with the tuffaceous, carbonate-rich composition of Tumbiana sediments (discussed below).



**Fig. 4.** pH effects on nitrogen isotopes. A: relative proportions of volatile ammonia ( $\text{NH}_3$ ) and aqueous ammonium ( $\text{NH}_4^+$ ) as a function of pH at 25 °C. B: isotopic composition of  $\text{NH}_4^+$  remaining in solution with progressive conversion to volatile  $\text{NH}_3$ . Grey lines mark average  $\delta^{15}\text{N}_{\text{bulk}}$  seen in the Tumbiana samples.



**Fig. 2.** Nitrogen isotope ratios through time. 'T11' = data from Thomazo et al. (2011). Light symbols are bulk samples, dark symbols of same color are kerogen isolates. Additional data supporting Figs. 2 and 3 were compiled from the literature (Algeo et al., 2013; Garvin et al., 2009; Godfrey and Falkowski, 2009; Godfrey et al., 2013; Kump et al., 2011; Papineau et al., 2005; Stüeken, 2013; Yamaguchi, 2002).



**Fig. 3.**  $\delta^{15}\text{N}$  versus  $\text{C}_{\text{org}}/\text{N}$  ratios. N is organic for kerogen isolates (darker symbols) and bulk for all others (lighter symbols). Red circles = bulk sediment data from modern and Eocene alkaline lakes (see text for references). Black open rectangle = bulk sediments from Holocene freshwater lakes (taken from Fig. S4c in McLauchlan et al., 2013). Symbols are the same as in Fig. 2.

$\text{NH}_4^+$  produced from degradation of organic matter dissociates to  $\text{H}^+$  and volatile  $\text{NH}_3$  with a  $\text{pK}_a$  of 9.24 at standard conditions (Fig. 4A). This dissociation imparts a large isotopic fractionation with residual  $\text{NH}_4^+$  becoming increasingly heavy (Fig. 4B). Li et al. (2012) observed an equilibrium fractionation of 45.4‰ at 23 °C between  $\text{NH}_4^+(\text{aq})$  and  $\text{NH}_3(\text{aq})$  (solid black line in Fig. 4B;

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