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# A secular increase in continental crust nitrogen during the Precambrian

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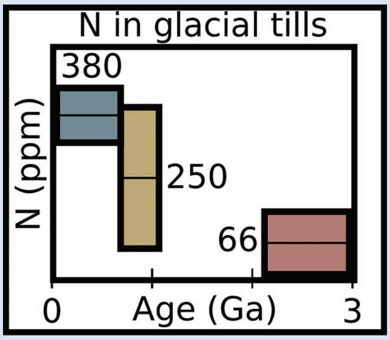
## Abstract




Recent work indicates the presence of substantial geologic nitrogen reservoirs in the mantle and continental crust. Importantly, this geologic nitrogen has exchanged between the atmosphere and the solid Earth over time. Changes in atmospheric nitrogen (*i.e.* atmospheric mass) have direct effects on climate and biological productivity. It is difficult to constrain, however, the evolution of the major nitrogen reservoirs through time. Here we show a secular increase in continental crust nitrogen through Earth history recorded in glacial tills (2.9 Ga to modern), which act as a proxy for average upper continental crust composition. Archean and earliest Palaeoproterozoic tills contain 66 ± 100 ppm nitrogen, whereas Neoproterozoic and Phanerozoic tills contain 290 ± 165 ppm nitrogen, whilst the isotopic composition has remained constant at ~4‰. Nitrogen has accumulated in the continental crust through time, likely sequestered from the atmosphere *via* biological fixation. Our findings support dynamic, non-steady state behaviour of nitrogen through time, and are consistent with net transfer of atmospheric N to geologic reservoirs over time.

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## Introduction

The evolution of the Earth System N cycle and the distribution of N in the Earth over the planet's history are not well constrained (Zerkle and Mikhail, 2017). Nitrogen moves between different reservoirs in the Earth system including the atmosphere, biosphere, and geosphere (Marty, 1995; Boyd, 2001; Busigny *et al.*, 2003, 2011). Changes in the distribution of N among the major reservoirs of the Earth (mantle, crust, and atmosphere) have direct effects on planetary habitability. Biologic productivity based on N-fixing can be limited under very low $N_2$ partial pressures (Klingler *et al.*, 1989), and the amount and speciation of N in the atmosphere affect temperature through direct or indirect greenhouse warming (Goldblatt *et al.*, 2009; Wordsworth and Pierrehumbert, 2013; Byrne and Goldblatt, 2015).

Higher $N_2$ atmospheres can enhance the effectiveness of greenhouse gases (Goldblatt *et al.*, 2009; Wordsworth and Pierrehumbert 2013), potentially providing a solution to the Faint Young Sun Paradox (Sagan and Mullen, 1972; Fuelner, 2012). Specifically, pressure-broadening (Goldblatt *et al.*, 2009) of $CO_2$ by an atmosphere with 2–3 fold more $N_2$ can provide warming consistent with constraints on atmospheric $CO_2$ content in the Archean (Sheldon, 2006). It is difficult to assess this, and other hypotheses of changing atmospheric mass (Som *et al.*, 2012, 2016; Barry and Hilton 2016), through direct measurements of palaeoatmospheric conditions. Another approach is to constrain the history of geologic N reservoirs.

One such reservoir is the continental crust. Current estimates for the amount of N in the modern continental crust range from 0.25 present atmospheric N mass (PAN, or $4 \times 10^{18}$ kg N) (Rudnick and Gao, 2014) to 0.5 PAN (Goldblatt *et al.*, 2009; Johnson and Goldblatt, 2015). These estimates rely on measurements of individual rock types, which are then weighted by their proportion in the crust. For comparison, estimates of N in the Earth's interior range from 1 to 7 PAN in the Bulk Silicate Earth and >50 PAN in the core (Johnson and Goldblatt, 2015, and references therein). Modern subducted N is estimated to be $5 \times 10^{-10}$ PAN *per* year (Johnson and Goldblatt, 2015) with non-arc outgassing of $1.75 \times 10^{-11}$ PAN *per* year (Cartigny and Marty, 2013). The estimates of crustal N content may be biased, though, due to the effects of differential chemical weathering and alteration. In addition, these approaches offer no temporal resolution. As an alternative approach, we present measurements of glacial tills through time as a proxy for the upper continental crust.

Large glaciers and ice sheets erode a wide variety of rock types, and resulting glacial till will represent an average composition of the crust over which they erode. Thus, integration of many samples of glacial till can act as a proxy for average upper continental crust composition. This approach was first utilised by Goldschmidt (1933), but has since been used to estimate the upper continental crust composition of both Phanerozoic, juvenile crust (Canil and Lacourse, 2011) as well as the composition of the crust through time (Gaschnig *et al.*, 2016). Physical weathering and erosion by a glacier should

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not impart any isotopic fractionation on the samples. In addition, while weathering can produce locally distinct $\delta^{15}N$ values (Boyd, 2001), it is expected that large glaciers will represent an average composition, which will integrate local variation.

While biologic N cycling (Gruber and Galloway, 2008) has been a topic of research for well over a hundred years (Breneman, 1889), the geologic N cycle and exchange of N between the atmosphere and solid Earth have received far less attention. Some modelling efforts suggested near steady state N concentrations in the crust, mantle, and atmosphere over at least the Phanerozoic (Berner, 2006), and possibly for most of Earth history (Zhang and Zindler, 1993; Tolstikhin and Marty, 1998). In contrast, geochemistry (Mitchell *et al*., 2010; Busigny *et al*., 2011; Barry and Hilton, 2016), other models (Hart, 1978; Stüeken *et al*., 2016), and physical proxies (Som *et al*., 2012, 2016; Kavanagh and Goldblatt, 2015) directly contradict the steady state hypothesis. The later proxies are consistent with movement of N between different reservoirs of the Earth and significant changes in the mass of the atmosphere over time. Additional thermodynamic calculations argue that the evolution of mantle redox and Eh-pH state at subduction zones directly affects $N_2$ outgassing, and therefore the distribution of N in the Earth through time (Mikhail and Sverjensky, 2014).

Either the distribution of N among the main reservoirs of the Earth (atmosphere, mantle, continental crust) has been in steady state over Earth history or it has been more dynamic. A difficulty in assessing the validity of steady state and dynamic interpretations of N distribution over Earth history is reconstructing N concentrations in geologic reservoirs in the past. The analysis of glacial tills presented herein suggests an increase in continental N through time, providing a temporal constraint on one of the three major N reservoirs of the Earth system.

## Nitrogen in Glacial Tills

We analysed a series of tills from Gaschnig *et al*. (2016) for N concentration and N isotopes. These till samples consisted of predominantly fine grained matrix material, and come from formations as old as 2.9 Ga to formations as young as 0.3 Ga. We have also included a younger till, Till-4, which is a standard provided by the Geological Survey of Canada.

Nitrogen concentrations are low in glacial tills during the Archean and earliest Palaeoproterozoic, moderate and variable during the Neoproterozoic, and moderate-high and less variable during the Phanerozoic (Fig. 1, Table 1, Supplementary Information). We define "low" as less than average granite, 54 ppm (Johnson and Goldblatt, 2015), "high" as approaching average upper crust sedimentary rocks, >400 ppm, and "moderate" as in between. Performing Student's t-test (Student, 1908) indicates that both the mean, shown with one standard deviation, Neoproterozoic (250 ± 180 ppm) and Phanerozoic (380 ± 50 ppm) concentrations are significantly different from the mean of the Archean and earliest Palaeoproterozoic (66 ± 100 ppm) samples. There appears to be a secular increase in N content in the continental crust through time.

**Table 1** Proportion of till samples in each age group that have high (>400 ppm), low (<54 ppm), and moderate (in between) N.

| Age | % low | % moderate | % high |
|---|---|---|---|
| Archean | 100 | 0 | 0 |
| Palaeoproterozoic | 75 | 25 | 0 |
| Neoproterozoic | 10 | 60 | 30 |
| Phanerozoic | 0 | 50 | 50 |

In contrast, mean (plus one standard deviation) $\delta^{15}N$ values remain constant within error for all samples, with a value of 3.5 ± 1.4 ‰ for the Archean and earliest Palaeoproterozoic, 4.9 ± 4.0 ‰ for Neoproterozoic, and 4.9 ± 2.6 ‰ for the Phanerozoic (Fig. 2). These three populations are not significantly different using Student's t-test. Such isotopic consistency implies either no biologic fractionation during weathering or consistent biologic involvement in glacial weathering through time.

The increase in N concentration through time does not appear to be the result of progressive alteration. There is no correlation between N concentration and $\delta^{15}N$, the chemical index of alteration (CIA), or Cs/Zr (see Supplementary Information). If N was being lost due to weathering or volatilisation, low N samples should have high $\delta^{15}N$ and CIA values. If N were behaving as a fluid-mobile element like Cs, there would be a correlation between N and Cs/Zr, with Zr being a non-fluid mobile element. Such lack of correlation indicates that changes in N concentration are not explained by progressive alteration through time.

Two of the low N samples from the Neoproterozoic may not be fully representative of general, contemporaneously formed, upper crust. One result is from erosion of 1.1 Ga Grenville-associated units (Konnarock Formation) and a second is heavily influenced by erosion of bimodal volcanism (Pocatello Formation) (Gaschnig *et al*., 2016). We suggest Grenvillian rocks may not be representative of the average upper crust, as they typically expose deeper crust from within an orogenic belt. Clasts in the Konnarock Formation are primarily middle to lower crustal granites (Rankin, 1993). Globally, granites average 54 ppm N (Johnson and Goldblatt, 2015), much lower than sedimentary or metasedimentary rocks. Though more sparsely measured, volcanic rocks tend to have low N as well, around 0.1 to 10 ppm (Johnson and Goldblatt, 2015), owing to the high volatility of N during the eruption of oxidised magma (Libourel *et al*., 2003). Tills that sample only igneous rocks may be biased towards low N.

Additionally, while there is a correlation between N concentration and Rb and K for low N samples, there is not for moderate and high N samples (Supplementary Information). Nitrogen is commonly found as $NH_4^+$ in geologic samples and substitutes for K in silicates (Honma and Itihara, 1981; Hall, 1999). Many studies have observed correlation between N, K, and Rb in metasediments (Bebout and Fogel, 1992; Busigny *et al*., 2003). Thus, low N samples suggest incorporation of metasedimentary N into the crust *via* recycling of N into the mantle at subduction zones (Marty 1995; Goldblatt *et al*., 2009; Busigny *et al*., 2011; Mikhail and Sverjensky, 2014; Barry and Hilton, 2016). Higher N samples imply an additional, or more efficient, transfer mechanism.

There appears to be a relationship between the present continent of the sample outcrop and N concentrations (Fig. 1). African samples appear to increase in the Palaeoproterozoic and remain high during the Neoproterozoic and Phanerozoic. In contrast, samples from North America are low-moderate into the Neoproterozoic with the most recent sample showing high N concentrations. The single sample from South America and both samples from Asia have moderate to high N. While the strongest control on N concentration appears to be age, it is possible that different continents have a different N history due to differences in their growth history (Supplementary Information). It is also possible that this apparent relationship between present-day geography and N concentration is simply an artefact of a small number of samples.

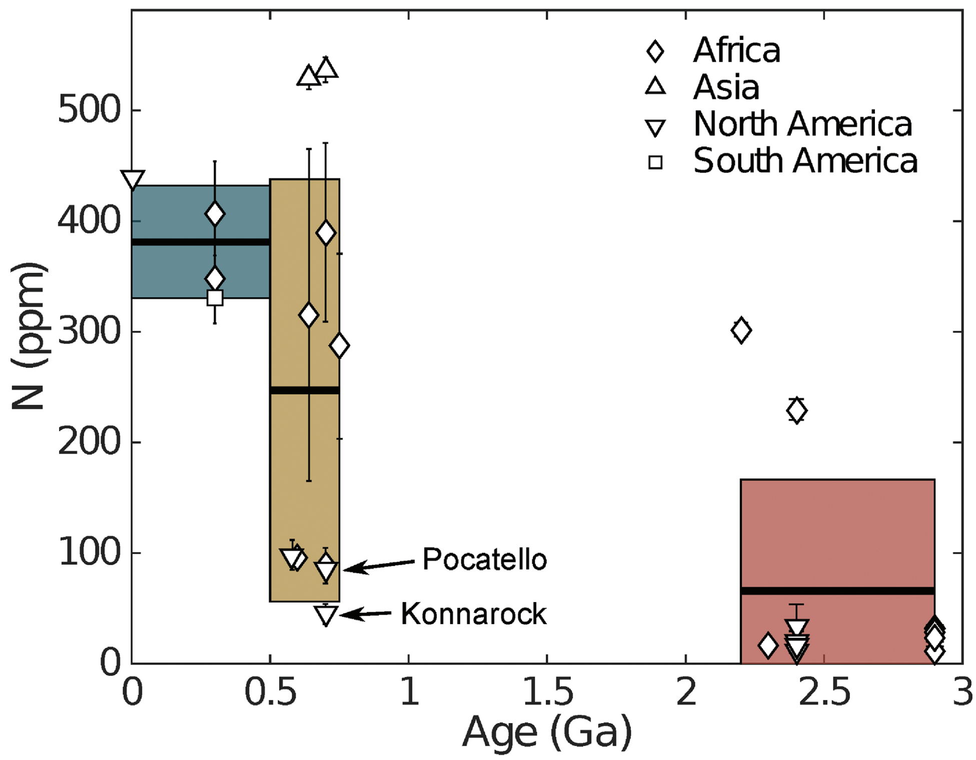


**Figure 1** Nitrogen concentration in glacial tills through time. Means of triplicate analyses of each sample, with standard deviation, are shown with shapes representing modern continent of exposure. Black lines and coloured boxes show mean and standard deviation of Archean-Palaeoproterozoic, Neoproterozoic, and Phanerozoic samples. Low N samples from units that have eroded primarily igneous terranes in North America are noted, and discussed in the text.

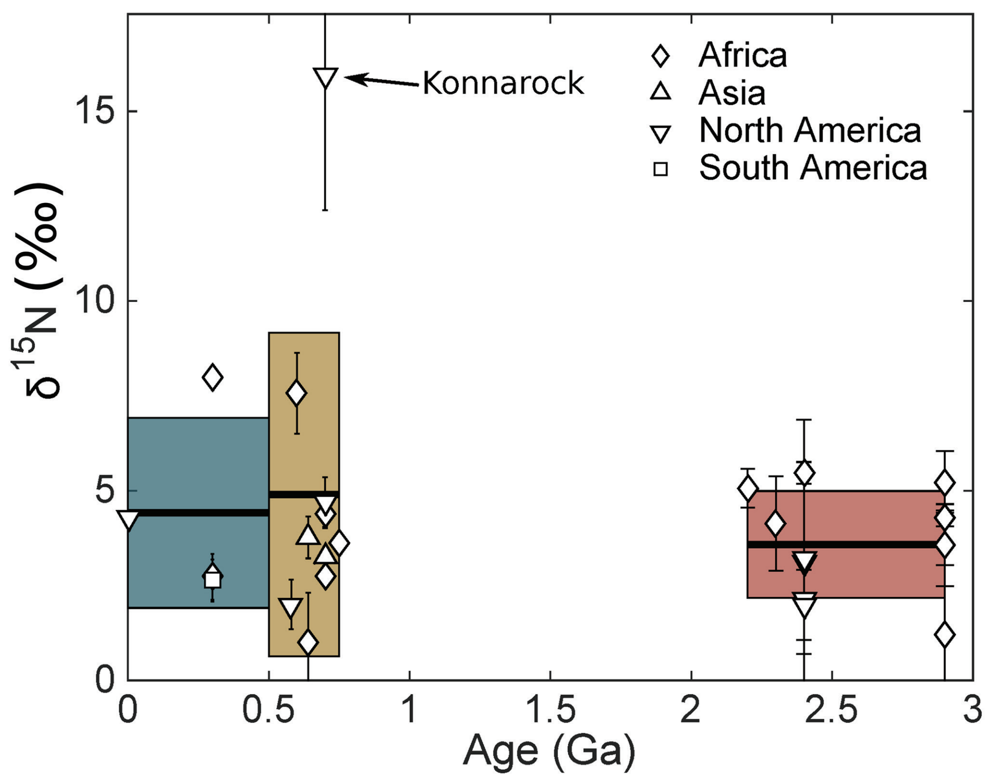


**Figure 2** Nitrogen isotope values (‰) in glacial tills through time. Averages (black lines) for each time period (Archean-Palaeoproterozoic, Neoproterozoic, and Phanerozoic) are equivalent within error (one standard deviation, coloured boxes), indicating no change in the isotopic character of the continental crust through time.

## Implications for Atmospheric Evolution

How, then, did N accumulate? The isotopic signature is consistent through the record, and is most similar to either modern average marine $NO_3^-$ or sedimentary N (+5 to +7 ‰). The till record is distinct from both the modern atmosphere (0 ‰) and the best estimate for the MORB-source mantle value of -5 ‰, (Marty, 1995). The parsimonious explanation would be incorporation of biologically processed N into the crust with time. Such processing implies N-fixing, thus this N is ultimately of atmospheric origin.

The mechanisms which transfer N into the continental crust through time are speculative, but have important implications for models of N distribution through time. The most concentrated reservoirs of continental N are in sedimentary and metasedimentary rocks (concentrations 400–500 ppm), with concentrations much higher than igneous rocks (*e.g.*, 54 ppm in granites, 0.1–10s ppm in basalts; Johnson and Goldblatt, 2015). One likely mechanism of transfer, then, is burial of biologically-processed N at continental margins followed by accretion. An additional mechanism could be input of N at subduction zones. Sparse N concentration and isotopic data suggests that granitic N content has increased through time (Supplementary Information). In addition, granitic samples show an increase in $\delta^{15}N$ values through time, consistent with enhanced incorporation of biologically processed N.

The exact timing of incorporation of N is also difficult to determine. There are no glacial deposits from the Mesoproterozoic, rendering this till-based approach ill-suited to this time period. Interestingly, there are two high-N (>200 ppm) samples from the Palaeoproterozoic. Gaschnig *et al*. (2016) note a distinct change in the composition of tills between the Archean and Palaeoproterozoic glaciations, reflecting a transition from greenstone/komatiite dominated Archean crust to more felsic crust in the Proterozoic. This trend is perhaps mirrored in some of the N analyses, with more felsic crust having higher N concentration.

Regardless of the timing of the increase of crustal N, we can compare the upper crust N budget from the till proxy to previous work. Johnson and Goldblatt (2015) suggest 150 ± 22 ppm N in the upper crust, while Rudnick and Gao (2014) suggest 83 ppm. We use a total continental crust mass of $2.28 \times 10^{22}$ kg (Laske *et al*., 2013), with the upper crust being 53 % of the total (Wedepohl, 1995). The Rudnick and Gao (2014) estimate of 83 ppm N yields $0.1 \times 10^{18}$ kg N (0.25 PAN) in the upper crust and 150 ppm from Johnson and Goldblatt (2015) suggests 0.5 PAN. Based on exposed and buried outcrop area, the upper continental crust is 28 % Phanerozoic, 31 % Neoproterozoic, 16 % Mesoproterozoic, 15 % Palaeoproterozoic, and 10 % Archean (Goodwin, 1991, 1996). Given this crust distribution, and assuming the Mesoproterozoic has the same N concentration as the Archean/Palaeoproterozoic, our work suggests an upper crust N concentration of 210 ppm, equivalent to $2.5 \times 10^{18}$ kg N, or 0.63 PAN (Table 2).

Importantly, the N content of the lower crust is poorly constrained, but could be a significant N reservoir as well. Johnson and Goldblatt (2015) suggest 17 ppm N in the lower crust, which would result in a total continental crust N concentration of 120 ppm and a N mass of $2.7 \times 10^{18}$ kg.

The trend of increased N concentration in the continental crust over time is consistent with non-steady state behaviour of N through Earth history. Specifically, the till record is consistent with net atmospheric drawdown through time (Goldblatt *et al*., 2009; Busigny *et al*., 2011; Barry and Hilton, 2016). While the tills provide a constraint on the evolution of one of the three major N reservoirs (continental crust), determining the exact evolution of the other two (mantle and atmosphere) requires more analyses. We cannot necessarily rule out modern or lower $pN_2$ at specific points in Earth history (*e.g.*, Som *et al*., 2012, 2016; Marty *et al*., 2013) but the till data is most consistent with higher atmospheric mass in the past. The balance of mantle outgassing at mid-ocean ridges and arcs to in-gassing at subduction zones is an important, and unconstrained, parameter, over Earth history. Strong net mantle outgassing would be required to have non-decreasing atmospheric N through time.

**Table 2** Distribution of upper continental crust ages after Goodwin (1991, 1996). We assume that tills accurately sample crust of each age, and that the Mesoproterozoic has the same N concentration as the Archean/Palaeoproterozoic.

| Age | % crust | N (ppm) |
|---|---|---|
| Phanerozoic | 28 | 380 |
| Neoproterozoic | 31 | 250 |
| Mesoproterozoic | 16 | 66 |
| Palaeoproterozoic | 15 | 66 |
| Archean | 10 | 66 |
| | *Total upper crust* [N] = 210 ppm | mass = $2.5 \times 10^{18}$ kg N |


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## Additional Information

**Supplementary Information** accompanies this letter at www.geochemicalperspectivesletters.org/article1731

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