

# EarthN: A new Earth System Nitrogen Model

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## Key Points:

- We model the evolution of nitrogen in all the reservoirs of Earth
- Total, non-core N and plate tectonics exert strong control on atmospheric mass
- Weathering and the Great Oxidation event cause atmospheric draw-down

## Abstract

The amount of nitrogen in the atmosphere, oceans, crust, and mantle have important ramifications for Earth's biologic and geologic history. Despite this importance, the history and cycling of nitrogen in the Earth system is poorly constrained over time. For example, various models and proxies contrastingly support atmospheric mass stasis, net outgassing, or net ingassing over time. In addition, the amount available to and processing of nitrogen by organisms is intricately linked with and provides feedbacks on oxygen and nutrient cycles. To investigate the Earth system nitrogen cycle over geologic history, we have constructed a new nitrogen cycle model: EarthN. This model is driven by mantle cooling, links biologic nitrogen cycling to phosphate and oxygen, and incorporates geologic and biologic fluxes. Model output is consistent with large (2-4x) changes in atmospheric mass over time, typically indicating atmospheric drawdown and nitrogen sequestration into the mantle and continental crust. Critical controls on nitrogen distribution include mantle cooling history, weathering, and the total Bulk Silicate Earth+atmosphere nitrogen budget. Linking the nitrogen cycle to phosphorous and oxygen levels, instead of carbon as has been previously done, provides new and more dynamic insight into the history of nitrogen on the planet.

## 1 Introduction

Despite its importance and abundance in the Earth system, relatively little is known about the cycling of N throughout the major reservoirs of the Earth through time [Zerkle and Mikhail, 2017]. This is an important component of the Earth system, as the amount of N in the atmosphere can directly affect the climate [Goldblatt *et al.*, 2009; Wordsworth and Pierrehumbert, 2013] as well as biologic productivity [Klingler *et al.*, 1989]. Recent work has challenged the notion that N is primarily an atmospheric species, and instead the solid Earth may actually hold the majority of the planet's N budget [Marty, 2012; Halliday, 2013; Johnson and Goldblatt, 2015; Barry and Hilton, 2016; Mallik *et al.*, 2018].

While the major biologic and geologic fluxes affecting N distribution are known, their behavior over Earth history is not constrained. Early descriptions of atmospheric N<sub>2</sub> in the Precambrian admitted lack of data prevented speculation on what the atmospheric, and therefore mantle and continental crust, N content was at that time and how it has evolved since [Delwiche, 1977]. Subsequent work generally supports three hypotheses: steady-state atmospheric N mass over time [Marty *et al.*, 2013], net mantle outgassing over time [Som *et al.*, 2012, 2016], and net ingassing over time [Nishizawa *et al.*, 2007;

41 *Goldblatt et al.*, 2009; *Johnson and Goldblatt*, 2015; *Barry and Hilton*, 2016; *Mallik et al.*,  
42 2018; *Yoshioka et al.*, 2018]. Importantly, the assumption that atmospheric mass should be  
43 constant over Earth history is not an inherent property of the planet.

44 Preliminary modelling efforts considered sedimentary rocks as the main geologic  
45 storage and recycling vector for N [*Zhang and Zindler*, 1993; *Berner*, 2006] and compared  
46 N geochemically to the noble gases or carbon [*Tolstikhin and Marty*, 1998]. These studies  
47 found that there was little change (< 1%) in atmospheric N<sub>2</sub> over at least the Phanero-  
48 zoic [*Berner*, 2006] and possibly the majority of Earth history [*Zhang and Zindler*, 1993].  
49 Additionally, while comparison to noble gases is valid for outgassing of oxidized mag-  
50 mas [*Libourel et al.*, 2003], this comparison is not valid at subduction boundaries, as N is  
51 mostly found as NH<sub>4</sub><sup>+</sup> in subducted sediments [*Bebout and Fogel*, 1992] and oceanic crust  
52 [*Busigny et al.*, 2011].

53 The geologic treatment of N in previous models may have missed some important  
54 behavior. Specifically, only considering sedimentary rocks as a sink for biologically pro-  
55 cessed N [*Berner*, 2006] based on N/C ratios does not include hydrothermal addition of  
56 N to oceanic crust (Fig. 1), which is observed in modern and older altered crust [e.g.,  
57 *Halama et al.*, 2014]. Sediment-only geologic N models also assume N and C behave  
58 similarly in subduction zones, which may not be true as N is likely found primarily as  
59 NH<sub>4</sub><sup>+</sup> geologically and C as organic C or CO<sub>3</sub><sup>2-</sup>. In addition, previous whole-Earth mod-  
60 eling [*Tolstikhin and Marty*, 1998] maintained a steady-state upper mantle, in terms of N-  
61 isotopes and concentration, by recycling of sedimentary and sea-water-sourced N from the  
62 surface and N from the lower mantle entrained in plumes. This approach is incomplete,  
63 as, again, surface N is subducted to the mantle as NH<sub>4</sub><sup>+</sup> and it is likely that the mantle as  
64 a whole is not layered. Therefore, a mechanism of “re-filling” the upper mantle from the  
65 lower mantle slowly over time appears untenable.

66 Studies of several modern subduction zones suggest more dynamic N evolution,  
67 and that there is overall net transport of N into the solid Earth, either the mantle or arc-  
68 generated crust. Importantly, the N that survives the subduction barrier seems to mostly  
69 reside in the oceanic crust [*Li et al.*, 2007; *Mitchell et al.*, 2010]. There are many possi-  
70 ble mineral hosts for such N, typically found as NH<sub>4</sub><sup>+</sup>, during subduction, including NH<sub>4</sub><sup>+</sup>-  
71 bearing feldspars, pyroxenes, beryls, and phlogopite in the mantle [*Watenphul et al.*, 2009,  
72 2010; *Bebout et al.*, 2015]. Such crystalline N in altered crust appears to be more likely

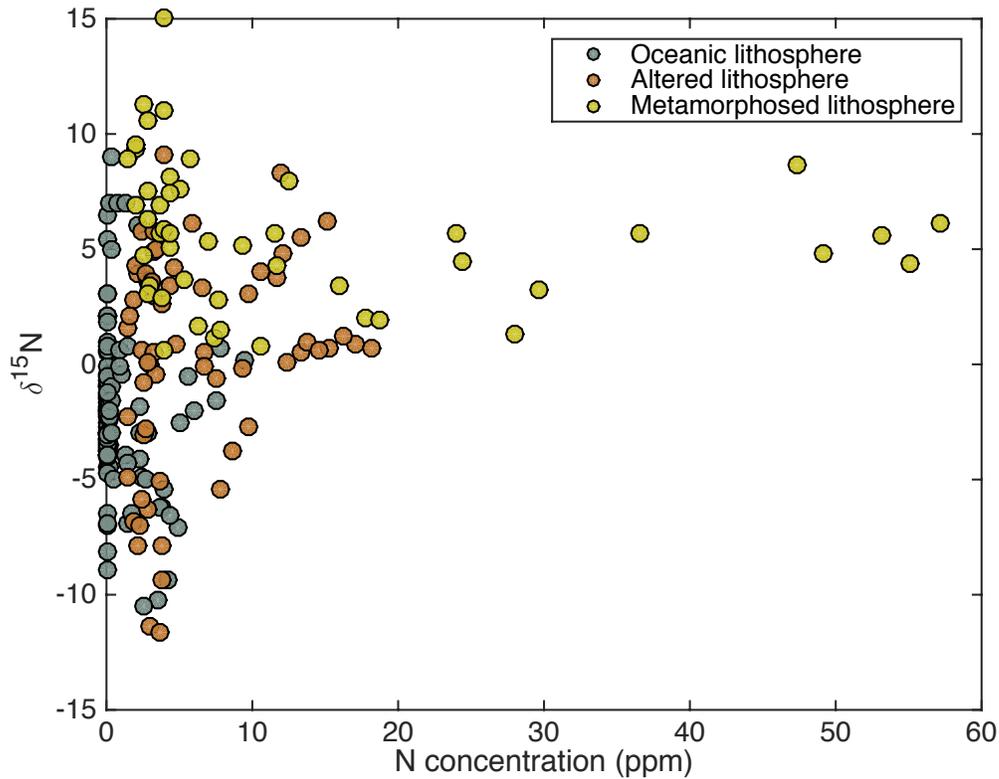


Figure 1:  $\delta^{15}\text{N}$  plotted against N concentration (ppm) for oceanic lithosphere. Data are from the compilation of *Johnson and Goldblatt* [2015]. Shown are values from fresh lithosphere, altered lithosphere, and metamorphosed. Altered lithosphere has experienced temperatures of  $<300\text{ }^{\circ}\text{C}$  and metamorphosed samples have experienced temperatures  $>300\text{ }^{\circ}\text{C}$ . As oceanic lithosphere experiences alteration, N concentration increases, and initially depleted  $\delta^{15}\text{N}$  values, with a mean of  $-1.8\text{‰}$  are enriched, indicating additional N is sourced from biologic material, which has  $\delta^{15}\text{N}$  of  $5\text{‰}$ . Altered lithosphere rocks include MORBs while metamorphosed lithosphere rocks include blueschists, eclogites, and metagabbros.

73 to be carried into the mantle, whereas sedimentary N tends to return to the atmosphere at  
74 subduction zones [Fischer *et al.*, 2002; Elkins *et al.*, 2006; Halama *et al.*, 2014].

75 As such, we are presented with a conundrum. Modeling efforts suggest that the at-  
76 mosphere and solid Earth have remained in equilibrium in terms of N-content over time.  
77 Contrastingly, geochemical evidence suggests there may be net transport of N from the  
78 surface to the mantle over time. It is from this conundrum that the construction of an  
79 Earth-system N cycle model, EarthN, follows.

80 Previous Earth system models implicitly have biologic processing [e.g., Stüeken  
81 *et al.*, 2016], but none so far actually explicitly model the behavior of organisms. Biologic  
82 productivity and activity is the gate-keeper between the atmosphere and the solid Earth.  
83 Similarly, recent work has modeled the nitrogen cycle but without biology [Laneville  
84 *et al.*, 2018], to serve as a background for interpretations and models including biology.  
85 Nitrogen can cycle throughout the atmosphere, biosphere, sedimentary rocks, and crys-  
86 talline Earth, thus constructing a model that integrates both biologic and geologic fluxes is  
87 critical for investigating the N-cycle over Earth history.

## 88 **2 Model setup**

89 The model is divided into a number of boxes. These are the atmosphere, three shal-  
90 low ocean boxes (low-latitude, high-latitude, shelf), deep ocean, two biologically active  
91 sediment boxes (reactive shelf, reactive deep), sediments not in communication with the  
92 ocean (shelf, deep), and geologic reservoirs (mantle, oceanic crust, continental crust).

93 The model contains N as  $N_2$ ,  $NO_3^-$ , and  $NH_4^+$ , the last of which can be in the ocean  
94 or in geologic reservoirs. We also include other biologically relevant species:  $PO_4^{3-}$  and  
95  $O_2$ , as well as inorganic tracers: K,  $^{40}K$ ,  $^{40}Ar$ , and  $^{36}Ar$ . Phosphate directly affects biologic  
96 productivity and  $O_2$  affects both productivity and which pathways of the biologic N cycle  
97 are in operation. Nitrogen is geochemically similar to K when found as  $NH_4^+$  and geochem-  
98 ically similar to Ar when found as  $N_2$ . As K and Ar are not biologically important ele-  
99 ments, they serve as both a calibration and validation of the purely physical aspects of the  
100 model (Appendix C: ).

101 Biogeochemical fluxes are after Fennel *et al.* [2005], with a number of updates.  
102 Most geologic fluxes are driven by mantle cooling history after Korenaga [2010] and  
103 Padhi *et al.* [2012], which produces estimates of mantle temperature, crust production, and

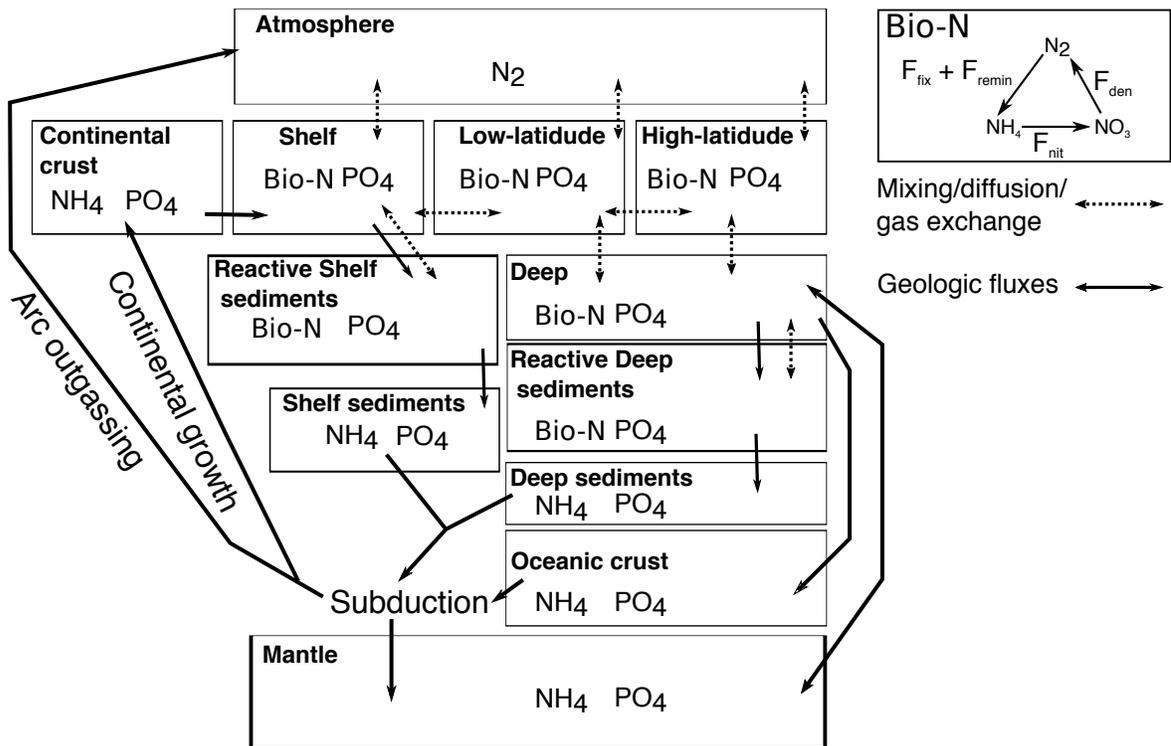


Figure 2: Earth system nitrogen cycle model schematic. In addition, we included K,  $^{40}K$ ,  $^{40}Ar$ ,  $^{36}Ar$ , and  $^{40}Ca$  as checks on non-biologic cycles, though these are not shown here.

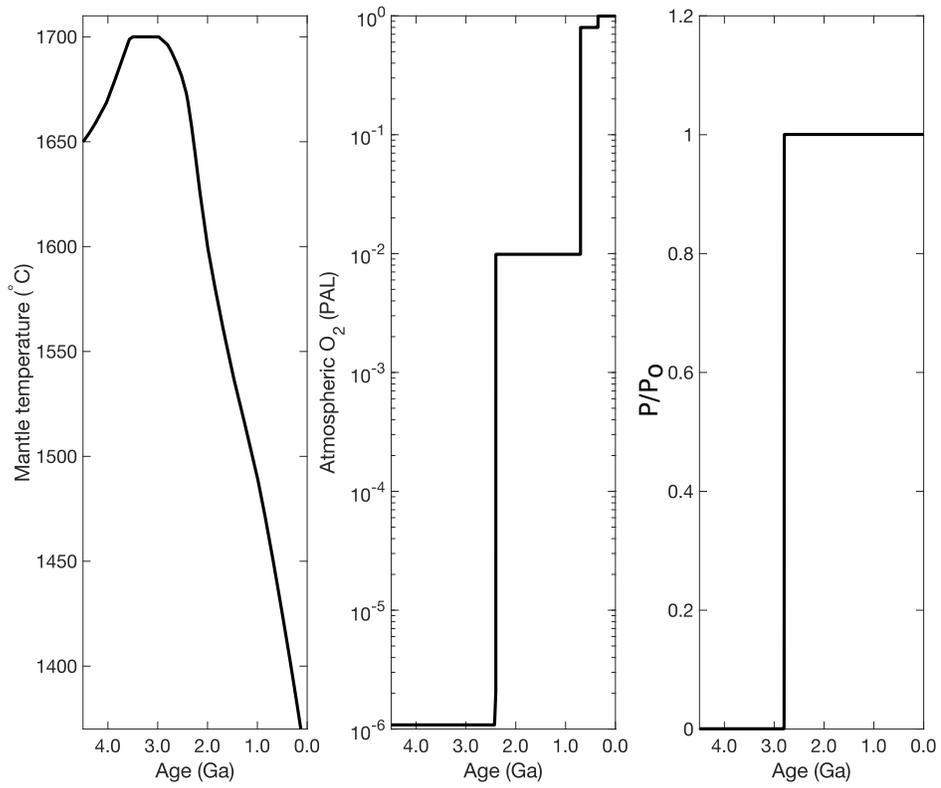


Figure 3: Model forcings, including average mantle potential temperature (°C) [Korenaga, 2010], atmospheric O<sub>2</sub> [e.g., Lyons *et al.*, 2014], and primary productivity (P) compared to modern (P<sub>0</sub>) constant [Goldblatt *et al.*, 2006].

104 spreading rate through time (Fig. 3). Some runs have a constant proportion of subducted  
105 material retained to the mantle, and some link subducted fraction to mantle temperature.

106 The following is first a brief description of element cycles, then a detailed descrip-  
107 tion of the model setup. We discuss each model box, the species contained within said  
108 box, and the fluxes that affect the amount of each species in the box. We use  $R_j^i$  to rep-  
109 resent reservoir in moles size of species  $j$  in box  $i$  and  $C_j^i$  to represent the corresponding  
110 concentration.  $F_k^i$  represents fluxes of type  $k$  in box  $i$  (Table 1). There are a number of  
111 fluxes that are sensitive to reactant concentration (e.g., Michaelis-Menten behavior), and  
112 are shown as  $v_l$  where  $l$  is specific to each sensitivity  $v$ . Parameter values are given in  
113 Table 2 and full differential equations are given in Appendix B.

## 114 2.1 Brief element cycle descriptions

115 The model Earth-system N cycle is as follows. Atmospheric  $N_2$  dissolves in the  
116 ocean, where it can be fixed (i.e., breaking the N triple bond) by bacteria. Fixed N then  
117 cycles biologically, and is released as waste or when organisms die. In oxygenated water,  
118 this reduced biologic N is quickly nitrified ( $NH_4^+$  to  $NO_3^-$ ) by bacteria; in anoxic water it  
119 remains as  $NH_4^+$ . Some organic material sinks into the deep ocean, where most gets rem-  
120 ineralized into either  $NH_4^+$  or  $NO_3^-$  depending on  $O_2$  levels, and a small portion sinks to  
121 the sediments. In the sediments, organic matter breaks down and bonds as  $NH_4^+$  into clays  
122 and other K-bearing minerals. Some N also gets incorporated into oceanic crust during  
123 hydrothermal alteration. Sediments and oceanic crust get subducted, with a portion of  
124 N going into the mantle, a portion outgassed to the atmosphere, and a portion incorpo-  
125 rated into arc-generated crust. Mantle N can be outgassed at mid-ocean ridges. Continen-  
126 tal crust N, organic or inorganic, can be weathered and added back to the ocean.

127 Phosphate enters the ocean due to continental weathering and from mid-ocean ridge  
128 outgassing. In the shallow ocean, it is consumed during primary production, both that  
129 based on already fixed N and that based on fixing new N. It is then exported to the deep  
130 or lower shelf ocean, where it is either remineralized or buried in sediments. Sedimentary  
131 and altered oceanic crust  $PO_4^{3-}$  can be subducted. A portion goes into the mantle, and a  
132 portion into the continental crust.

133 The model cycles for K and Ar are only affected by physical, non-biologic process-  
134 ing. All isotopes of both elements mix between ocean boxes, and  $^{40}K$  decays to  $^{40}Ar$  in

135 every box where it is found. Continental weathering releases K to the shelf ocean, and Ar  
 136 to the atmosphere. Air sea gas exchange moves Ar from the surface ocean boxes to the  
 137 atmosphere. Both species can get incorporated into oceanic crust during hydrothermal al-  
 138 teration, and K can be incorporated into sediments. Again, during subduction, some K and  
 139 Ar is transported to the mantle, and the remainder either goes to the continental crust (K)  
 140 or the atmosphere (Ar). Both are added to the deep ocean during mid-ocean ridge out-  
 141 gassing.

## 142 2.2 <sup>40</sup>K-decay

143 Radioactive decay of <sup>40</sup>K produces <sup>40</sup>Ar in all boxes where <sup>40</sup>K is present:

$$144 F_{rd}^i = \lambda X_{40K} R_{40K}^i \quad (1)$$

145 for  $i = \{\text{all ocean and geologic boxes}\}$  where  $X_{40K}$  is the proportion of decays that form <sup>40</sup>Ar  
 146 and  $\lambda$  is the decay constant of <sup>40</sup>K.

## 147 2.3 Atmosphere

148 The atmosphere contains N<sub>2</sub>, O<sub>2</sub>, and both isotopes of Ar. N<sub>2</sub>, <sup>40</sup>Ar, and <sup>36</sup>Ar ex-  
 149 change with the ocean following stagnant-lid gas exchange [Liss and Slater, 1974], with  
 150 fluxes positive in the direction of sea to air:

$$151 F_{as}^i = u_{i,j} A^i (C_j^i - H_j P_j) \quad (2)$$

152 for boxes  $i = \{\text{low, high, shelf}\}$  oceans and species  $j = \{\text{N}_2, {}^{40}\text{Ar}, {}^{36}\text{Ar}, \text{O}_2\}$ .  $u_{i,j}$  is piston  
 153 velocity in m yr<sup>-1</sup> calculated by dividing the diffusion constant ( $D_i$ ) by thickness of stag-  
 154 nant boundary ( $z_{\text{film}}$ );  $A^i$  is ocean box surface area (m<sup>2</sup>);  $C_j^i$  is concentration of species  $j$   
 155 in box  $i$ ;  $H_j$  is Henry's law constant for species  $j$  (mol L<sup>-1</sup> atm<sup>-1</sup>); and  $P_j$  is partial pres-  
 156 sure of gas  $j$ , calculated as:

$$157 P_j = \frac{R_j^{\text{atm}}}{n_a} \quad (3)$$

158 where  $n_a$  is the number of moles corresponding to one atmosphere pressure (Table 2).

159 Gasses are also added to the atmosphere via outgassing at arcs and both isotopes of  
 160 Ar are added from continental crust weathering (Sec. 2.5).

Table 1: Full list of fluxes used in model. Shown are flux symbol, brief description, and which model species are affected by each flux. In ocean boxes (low, high, shelf, deep), all species includes  $\text{NO}_3^-$  and  $\text{NH}_4^+$ , while in geologic boxes, all species just includes moles of N.

<b>Flux</b>	<b>Description</b>	<b>Species affected</b>
$F_{\text{rd}}$	radioactive decay	$^{40}\text{Ar}$ , $^{40}\text{K}$
$F_{\text{as}}$	air-sea gas exchange	$^{40}\text{Ar}$ , $^{36}\text{Ar}$ , $\text{N}_2$
$F_{\text{mix}}$	water-mixing	all species
$F_{\text{nit}}$	nitrification	$\text{NO}_3^-$ , $\text{NH}_4^+$
$F_{\text{denit}}$	denitrification	$\text{NO}_3^-$ , $\text{N}_2$
$F_{\text{oldN}}$	production from fixed N	$\text{NO}_3^-$ , $\text{NH}_4^+$ , $\text{PO}_4^{3-}$
$F_{\text{newN}}$	production from newly fixed N	$\text{N}_2$ , $\text{PO}_4^{3-}$
$F_{\text{out}}$	export from shallow ocean boxes	$\text{NO}_3^-$ , $\text{NH}_4^+$ , $\text{N}_2$ , $\text{PO}_4^{3-}$
$F_{\text{remin}}$	reminalization in shelf and deep	$\text{NO}_3^-$ , $\text{NH}_4^+$ , $\text{PO}_4^{3-}$
$F_{\text{bur}}$	burial in sediments	$\text{N}$ , $\text{PO}_4^{3-}$
$F_{\text{seddif}}$	diffusion into sediments, out of water	$\text{NH}_4^+$
$F_{\text{sub}}$	subduction of crust and sediments	all species
$F_{\text{subT}}$	total subduction	all species
$F_{\text{subnet}}$	net subduction	all species
$F_{\text{hydro}}$	hydrothermal alteration	all species
$F_{\text{w}}$	weathering	all species
$F_{\text{cg}}$	continental growth	all species
$F_{\text{scg}}$	continental growth from shelf sediments	all species
$F_{\text{ogarc}}$	outgassing-arcs	all species
$F_{\text{ogmor}}$	outgassing-mid ocean ridge	all species

161 Oxygen levels are prescribed. Levels start at  $10^{-6}$  present atmospheric level (PAL  
 162 =  $2 \times 10^{19}$  mol) through the Hadean and Archean. Atmospheric  $O_2$  increases to 0.01  
 163 PAL over 100 Myr at 2.4 Ga, then to 0.8 PAL at 0.630 Ga (beginning of the Ediacaran).  
 164 Oxygen rises to modern levels at 0.418 Ga (Devonian). Surface ocean  $O_2$  concentrations  
 165 are calculated assuming a Henry's law equilibrium.

## 166 2.4 Ocean

167 The ocean is divided into four boxes: high- and low-latitude shallow ocean, shelf  
 168 ocean, and deep ocean. All species in the model exist in the ocean. There are a number  
 169 of fluxes, both physical and biogeochemical that occur. Some can occur in all boxes, and  
 170 some only in specific boxes. Broadly, primary production occurs in shallow ocean boxes,  
 171 remineralization and burial occur in deep and shelf boxes, and nitrification and denitrifica-  
 172 tion occur in all boxes.

### 173 2.4.1 All boxes

174 There is physical water mixing between all ocean boxes. Mixing out of an ocean  
 175 box is simply the product of concentration of species  $j$  in box  $i$  and the sum of the water  
 176 fluxes ( $\Delta^{i-i^*}$ , in  $L yr^{-1}$ ) between box  $i$  and all other boxes ( $i^*$ ). Mixing in to box  $i$  is the  
 177 sum of the product of the concentrations of species  $j$  in each other box ( $i^*$ ) and the water  
 178 flux between box  $i$  and each other box ( $\Delta^{i-i^*}$ ):

$$179 F_{\text{mix},j}^i = -C_j^i \sum_{i^*} \Delta^{i-i^*} + \sum_{i^*} C_j^{i^*} \Delta^{i-i^*} \quad (4)$$

180 If, for example,  $i = \{\text{low}\}$ , then  $i^* = \{\text{high, shelf, deep}\}$ , and  $\Delta^{i-i^*}$  is mixing between low  
 181 and high, low and shelf, and low and deep boxes.

182 Nitrification occurs in all boxes. The rate of nitrification is dependent on  $O_2$  and  
 183  $NH_4^+$  concentrations:

$$184 v_{\text{Onit}}^i = \frac{C_{O_2}^i}{C_{O_2}^i + K_{\text{Oni}}} \quad (5)$$

$$185 v_{\text{NOit}}^i = \frac{C_{NH_4}^i}{C_{NH_4}^i + K_{\text{Nni}}} \quad (6)$$

186 The full equation can be parameterized as:

$$187 \quad F_{\text{nit}}^i = \mu_{\text{NH}_4} v_{\text{O}_{\text{nit}}}^i v_{\text{NH}_{\text{nit}}}^i R_{\text{NH}_4}^i \quad (7)$$

188 for box  $i = \{\text{low, high, shelf, deep}\}$ , and where  $K_{\text{O}_{\text{ni}}}$  is the half-saturation uptake concen-  
189 tration of  $\text{O}_2$  used in nitrification ( $20 \mu\text{M}$ ),  $K_{\text{N}_{\text{ni}}}$  is half-saturation uptake concentration of  
190  $\text{O}_2$  used in nitrification ( $100 \mu\text{M}$ ), and  $\mu_{\text{NH}_4}$  is a rate constant ( $\text{yr}^{-1}$ ).

191 Denitrification can also occur in every ocean box ( $i = \{\text{low, high, shelf, deep}\}$ ). It  
192 has been observed to follow first-order rate kinetics, with a half-saturation  $\text{NO}_3^-$  concentra-  
193 tion ( $K_{\text{d}}$ ) of  $8 \mu\text{M}$  [Goering, 1985; Evrard *et al.*, 2013]:

$$194 \quad v_{\text{NOde}}^i = \frac{C_{\text{NO}_3}^i}{C_{\text{NO}_3}^i + K_{\text{d}}} \quad (8)$$

195 In contrast to nitrification, denitrification only occurs at low  $\text{O}_2$  levels [Crowe *et al.*,  
196 2012; Dalsgaard *et al.*, 2014], herein parameterized as a Michaelis-Menten type reaction:

$$197 \quad v_{\text{Ode}}^i = \frac{C_{\text{O}_2}^i}{C_{\text{O}_2}^i + O_{\text{inhib}}} \quad (9)$$

198 where  $O_{\text{inhib}}$  is  $205 \text{ nM}$  [Dalsgaard *et al.*, 2014]. Thus, we parameterize denitrification as:

$$200 \quad F_{\text{den}}^i = (1 - v_{\text{Ode}}^i) v_{\text{NOde}}^i R_{\text{NO}_3}^i \quad (10)$$

#### 201 **2.4.2 Shallow ocean**

202 Primary production occurs in all shallow ocean boxes ( $i = \{\text{low, high, shelf}\}$ ). There  
203 are two types of productivity [Fennel *et al.*, 2005]: that based on already fixed N ( $F_{\text{oldN}}$ )  
204 and that based on newly-fixed  $\text{N}_2$  ( $F_{\text{newN}}$ ). These two fluxes together equal total export  
205 production ( $F_{\text{ExT}}^i$ ). The proportion of  $F_{\text{oldN}}$  to  $F_{\text{newN}}$  depends, in part, on the N:P ratio,  
206 which we assume will always move towards Redfield (i.e., 16:1). We parameterize this  
207 relationship as:

$$208 \quad L_{\text{R}}^i = \frac{N/P^i}{N/P^i + K_{\text{NP}}} \quad (11)$$

209 where  $K_{\text{NP}}$  is 8.

210 In addition,  $F_{\text{oldN}}$  can be  $\text{PO}_4^{3-}$  or N-limited:

$$211 \quad L_{\text{N}}^i = \frac{N_{\text{all}}^i}{N_{\text{all}}^i + K_{\text{N}}} \quad (12)$$

$$212 \quad L_{\text{P}}^i = \frac{C_{\text{PO4}}^i}{C_{\text{PO4}}^i + K_{\text{P}}} \quad (13)$$

213 where  $K_{\text{N}}$  and  $K_{\text{P}}$  are the half saturation uptake values for N and  $\text{PO}_4^{3-}$ .  $N_{\text{all}}^i$  is the sum of  
 214  $C_{\text{NH4}}^i$  and  $C_{\text{NO3}}^i$  in box  $i$ . We also assume productivity ( $P$ ) was 1000 times less efficient  
 215 before the evolution of oxygenic photosynthesis:

$$216 \quad \frac{P}{P_o} = ((1 + 1 \times 10^{-3}) + \tanh((t - \text{Phot}_{\text{On}})/0.1)) \times 0.5; \quad (14)$$

217 where  $P_o$  is modern primary productivity efficiency (1) and  $\text{Phot}_{\text{On}}$  is the age of oxygenic  
 218 photosynthesis evolution.

219 Thus,  $F_{\text{oldN}}^i$  is:

$$220 \quad F_{\text{oldN}}^i = \frac{P}{P_o} L_{\text{R}}^i L_{\text{N}}^i L_{\text{P}}^i R_{\text{PO4}}^i / \tau_{\text{prod}} \quad (15)$$

221 for boxes  $i = \{\text{low, high, shelf}\}$  and where  $\tau_{\text{prod}}$  is a production timescale, set to 0.5 yr.

222 Production from  $\text{N}_2$  fixing is  $\text{PO}_4^{3-}$ -limited, but also depends on N-concentrations  
 223 and partial pressure of  $\text{N}_2$ . There is a Michaelis-Menten relationship to partial pressure  
 224 [Klingler *et al.*, 1989]:

$$225 \quad v_{\text{fix}} = \frac{R_{\text{N2}}^{\text{atm}}}{R_{\text{N2}}^{\text{atm}} + K_{\text{f}}}; \quad (16)$$

226 where  $K_{\text{f}}$  is  $9.87 \times 10^{18}$  moles, or about the equivalent of 50 mbar pressure.

227 Thus, total production based on newly-fixed  $\text{N}_2$  is:

$$228 \quad F_{\text{newN}}^i = \frac{P}{P_o} (1 - L_{\text{R}}^i) L_{\text{P}}^i v_{\text{fix}} R_{\text{PO}}^i / \tau_{\text{prod}} \quad (17)$$

229 We note that we do not include abiotic N-fixing in our model [e.g., Navarro-González  
 230 *et al.*, 2001]. Total export production ( $F_{\text{EXT}}^i$ ) from boxes  $i = \{\text{low, high, shelf}\}$  is the sum  
 231 of  $F_{\text{oldN}}^i$  and  $F_{\text{newN}}^i$ . Export production in both the low- and high-latitude boxes go to the

232 deep ocean, and shelf export stays in the shelf box. Phosphate loss ( $F_{\text{out,PO4}}^i$ ) from shallow  
 233 boxes is equal to  $F_{\text{EXT}}^i$ . Fixed  $\text{NO}_3^-$  and  $\text{NH}_4^+$  losses are equal to:

$$234 \quad F_{\text{out},j}^i = 16F_{\text{oldN}}^i \frac{C_j^i}{N_{\text{all}}^i} \quad (18)$$

235 for  $j = \{\text{NO}_3^-, \text{NH}_4^+\}$  and  $\text{N}_2$  loss is:

$$236 \quad F_{\text{out,N}_2}^i = 16F_{\text{newN}}^i \quad (19)$$

237 as we keep track of moles N, not moles  $\text{N}_2$ .

### 238 **2.4.3 Shelf ocean, deep ocean, reactive shelf and deep sediments**

239  $\text{PO}_4^{3-}$  and N can be remineralized or buried, and K can be buried in sediments. The  
 240 efficiency of remineralization depends on oxygen concentration:

$$241 \quad f_{\text{aerobic}}^i = \frac{C_{\text{O}_2}^i}{C_{\text{O}_2}^i + K_{\text{O}}} \quad (20)$$

$$242 \quad F_{\text{reminfrac},j}^i = 0.9f_{\text{aerobic}}^i + 0.7(1 - f_{\text{aerobic}}^i). \quad (21)$$

243 for boxes  $i = \{\text{shelf ocean, deep ocean, reactive shelf sediments, reactive deep sediments}\}$   
 244 and species  $j = \{\text{PO}_4^{3-}, \text{NH}_4^+\}$  and where  $K_{\text{O}}$  is  $50 \mu\text{M}$ . The values in the above equations  
 245 are tuned to have aerobic remineralization convert 90% of export production, while only  
 246 70% gets remineralized under anaerobic conditions. Nitrogen remineralization and burial  
 247 is assumed to be in Redfield ratio (i.e., 16:1) compared to  $\text{PO}_4^{3-}$ . Nitrogen is remineralized  
 248 as  $\text{NH}_4^+$ .

249 Export production from the high and low-latitude shallow boxes is remineralized  
 250 in the deep ocean and export production in the shelf ocean is remineralized in the shelf  
 251 ocean. That which is not remineralized in the deep or shelf ocean boxes goes to the reac-  
 252 tive deep and shelf sediments, respectively. Remineralization can occur in these reactive  
 253 sediment boxes, with anything not remineralized buried to the non-reactive deep and shelf  
 254 sediments. Additionally, nitrification, denitrification, and diffusion occur in the reactive  
 255 sediment layers. Diffusion ( $F_{\text{diff}}^i$ ) is parameterized as:

$$256 \quad F_{\text{diff},j}^i = D_j \left( C_{\text{O}_2,j}^{i*} - \frac{C_{\text{O}_2,j}^i}{D_{\text{length}}} \right) SA^{i*} \quad (22)$$

257

for boxes  $i = \{\text{Reactive shelf sediments, reactive deep sediments}\}$  and  $i^* = \{\text{shelf ocean, deep ocean}\}$ .

258

 $D_j$  is the diffusion constant and  $D_{\text{length}}$  is diffusive length, which is set to 0.01 m.

Table 2: All model constants, shown with references. References are: H14 [Haynes et al., 2014], S99 [Sander, 1999], F05 [Fennel et al., 2005], LS74 [Liss and Slater, 1974], B16 [Bristow et al., 2016], D14 [Dalsgaard et al., 2014], G85 [Goering, 1985], E13 [Evrard et al., 2013], K89 [Klingler et al., 1989], JG15 [Johnson and Goldblatt, 2015], W10 [Winter, 2001], and K10 [Korenaga, 2010]

Parameter	Definition	Value	Reference
$\lambda$	decay constant of $^{40}\text{K}$ ( $\text{yr}^{-1}$ )	$5.543 \times 10^{-10} \text{ yr}^{-1}$	H14
$X_{40}$	fraction of decay producing $^{40}\text{Ar}$	0.1072	H14
$D_{\text{N}_2}$	Diffusion constants ( $\text{cm}^2 \text{ s}^{-1}$ )	$1.88 \times 10^{-5}$	H14
$D_{\text{Ar}}$		$1.88 \times 10^{-5}$	H14
$D_{\text{O}_2}$		$2.5 \times 10^{-5}$	H14
$D_{\text{length}}$	Diffusion length	0.01 m	
$H_{\text{N}_2}$	Henry's law constants ( $\text{mol L}^{-1} \text{ atm}^{-1}$ )	$1.3 \times 10^{-3}$	S99
$H_{\text{Ar}}$		$6.1 \times 10^{-4}$	S99
$H_{\text{O}_2}$		$6.1 \times 10^{-4}$	S99
$n_a$	moles equal to one atm pressure	$1.72 \times 10^{20}$	this study
$d$	ocean depth (m)	4500	F05
$z_{\text{film}}$	stagnant lid thickness (m)	$1.5 \times 10^{-5}$	LS74
$A^{\text{high}}$	ocean box surface area ( $\text{m}^2$ )	$2.3 \times 10^{12}$	F05
$A^{\text{low}}$		$2.3 \times 10^{12}$	F05
$A^{\text{shelf}}$		$5.1 \times 10^{11}$	F05
$V^{\text{high}}$	ocean box volumes (L)	$9 \times 10^{18}$	F05
$V^{\text{low}}$		$9 \times 10^{18}$	F05
$V^{\text{shelf}}$		$1.5 \times 10^{18}$	F05
$V^{\text{deep}}$		$8.1 \times 10^{20}$	F05
$\Delta^{\text{low-high}}$	mixing between ocean boxes (Sv)	30	F05
$\Delta^{\text{low-shelf}}$		30	F05
$\Delta^{\text{low-deep}}$		30	F05
$\Delta^{\text{high-shelf}}$		30	F05

Continued on next page

**Table 2 Model Constants – continued from previous page**

Parameter	Definition	Value	Reference
$\Delta^{\text{high-deep}}$		50	F05
$\Delta^{\text{shelf-deep}}$		5-100	This study
$K_{\text{Oni}}$	half-saturation uptake of $\text{O}_2$ in nitrification	283 nM	B16
$K_{\text{Nni}}$	half-saturation uptake of $\text{NH}_4^+$ in nitrification	100 $\mu\text{M}$	F05
$K_{\text{d}}$	half-saturation uptake of $\text{NO}_3^-$ in denitrification	8 $\mu\text{M}$	
$K_{\text{NP}}$	Redfield term	8.47 $\mu\text{M}$	G85, E13
$K_{\text{N}}$	half-saturation uptake of total N	1.6 $\mu\text{M}$	F05
$K_{\text{P}}$	half-saturation uptake of $\text{PO}_4^{3-}$	0.1 $\mu\text{M}$	F05
$K_{\text{f}}$	half-saturation uptake of $\text{N}_2$ during fixing	$9.87 \times 10^{18}$ mol	K89
$K_{\text{O}}$	$\text{O}_2$ concentration term	50 $\mu\text{M}$	
$K_{\text{dist}}$	percent of species extracted during MORB-genesis	0.90	
$\tau_{\text{prod}}$	Export production time-scale	0.5 $\text{yr}^{-1}$	
$\tau_{\text{W}}$	rate constant of weathering	$3.33 \times 10^{-9}$ $\text{yr}^{-1}$	
$\tau_{\text{scg}}$	rate constant of	$1 \times 10^{-8}$ $\text{yr}^{-1}$	this study
$\mu_{\text{NH4i}}$	nitrification rate constant	1 $\text{yr}^{-1}$	F05
$\text{O}_{\text{inhib}}$	Oxygen inhibition for denitrification	205 nM	D14
$u_{\text{co}}$	Modern spreading rate	0.05 $\text{m yr}^{-1}$	K10
$T_{\text{o}}$	Modern mantle potential temperature	1350 $^{\circ}\text{C}$	K10
$\rho_{\text{c}}$	Ocean crust density	3000 $\text{kg m}^{-3}$	
$M^{\text{desed}}$	mass of deep sediments	$7.3 \times 10^{23}$ g	JG15
$M^{\text{occrust}}$	mass of ocean crust	$5.4 \times 10^{24}$ g	JG15
$M^{\text{mantle}}$	mass of mantle shelf sediments to cont. crust	$4 \times 10^{27}$ g	JG15
$a_{\text{W}}$	Anoxic weathering fraction	0.1	this study
$k_{\text{weath}}$	Weathering rate $\text{O}_2$ dependence	$1 \times 10^{-3}$	this study
$V_{\text{hydro}}$	hydrothermal circulation volume	1.6 Sv	this study
$\text{Heff}$	Hydrothermal retention efficiency	0.1-1, varies by species	this study
$P_{\text{m}}$	percent partial melt during MORB-genesis	10%	W01

*Continued on next page*

**Table 2 Model Constants – continued from previous page**

Parameter	Definition	Value	Reference
$S$	spreading rate (m yr <sup>-1</sup> )	varies	K10
$h_{\text{sed}}$	sediment thickness	500 m	this study
$h_c$	Ocean crust thickness	16000 to 8000 m	K10
$L_s$	length of subduction zones	$4 \times 10^7$ m	this study
$L_r$	length of mid-ocean ridges	$8 \times 10^7$ m	this study
$f_{\text{shsed}}$	fraction shelf sediments subducted	$1 \times 10^{-9}$	this study
$f_{\text{Ncgarc}}$	fraction N added to continental crust	0.5	this study

259

## 260 2.5 Geologic model

261 The model is driven by a mantle cooling history from *Korenaga* [2010] and *Padhi*  
 262 *et al.* [2012]. This model suggests that mantle temperatures ( $T_m$ ) increased through the  
 263 early Archean, reached their peak in the middle Archean, and have been decreasing to  
 264 the modern day (Table 3, Fig. 3). Heat flux ( $Q$ ) followed a distinct evolution, reaching  
 265 its maximum later than the mantle temperature apex (Table 3). Temperature and heat flux  
 266 are used to parameterize a plate velocity ( $u_c$ ):

$$267 \quad u_c = u_{co} \frac{Q}{Q_o} \left( \frac{T_o}{T_m} \right)^2 \quad (23)$$

268 where  $u_{co}$ ,  $Q_o$ , and  $T_o$  are modern plate velocity (0.05 m yr<sup>-1</sup>), heat flux (39 TW), and  
 269 average mantle temperature (1350 °C).

270 The model then calculates crust production at mid-ocean ridges by combining spread-  
 271 ing rate with ridge length ( $L_r$ , m) and crust thickness ( $h_c$ , m):

$$272 \quad O_p = u_c h_c L_r \rho_c \quad (24)$$

273 where  $\rho_c$  is crust density (kg m<sup>-3</sup>), and  $h_c$  decreases linearly through time [*Sleep and*  
 274 *Windley*, 1982] from 16 km at the beginning of the model to 8 km at  $t = 4.5$  Gyr. We  
 275 assume that the amount of crust subducted ( $O_s$ ) is equal to  $O_p$ .

Table 3: Mantle temperature ( $T_m$ ) history, heat flux ( $Q$ ), and spreading rate ( $u_c$ ) evolution from *Korenaga [2010]; Padhi et al. [2012]*.

Age (Ga)	$T_m$ (°C)	$Q$ (TW)	$u_c$ (cm yr <sup>-1</sup> )
0	1350	39	5.00
0.5	1425	43	5.55
1.0	1490	41	4.68
1.5	1540	40	4.22
2.0	1600	39	3.75
2.5	1680	38	3.28
3.0	1700	37	3.05
3.5	1700	37	3.05
4.0	1670	37.5	3.23
4.5	1650	38	3.38

276

277

## 2.6 Sediments

278

Anything that does not get remineralized in the reactive sediment boxes gets buried

279

( $F_{\text{bur}}^i$ ) in sediments:

280

$$F_{\text{bur}}^i = F_{\text{burial}}^{i*} - F_{\text{remin}}^{i*} \quad (25)$$

281

for boxes  $i = \{\text{shelf sediments, deep sediments}\}$  and  $i^* = \{\text{reactive shelf sediments, reactive deep sediments}\}$ .

282

Species are subducted from both deep and shelf sediments. A constant fraction of

283

shelf sediment species gets subducted,:

284

$$F_{\text{subj}}^{\text{shsed}} = f_{\text{shsed}} R_j^{\text{shsed}} \quad (26)$$

285 where  $f_{\text{shsed}}$  is the fraction of shelf sediments that subduct ( $1 \times 10^{-9} \text{ yr}^{-1}$ ). Deep sediments  
286 subducted are equal to:

$$287 \quad F_{\text{sub},j}^{\text{dsed}} = \frac{m_{\text{sub}}^{\text{dsed}} R_j^{\text{dsed}}}{M^{\text{dsed}}} \quad (27)$$

288 where  $m^{\text{dsed}}$  is the mass of deep sediments subducted and  $M^{\text{dsed}}$  is the mass of deep sedi-  
289 ments ( $7.4 \times 10^{23} \text{ g}$ ). Mass of sediments subducted is:

$$290 \quad m_{\text{sub}}^{\text{dsed}} = L_s S h_{\text{sed}} \rho_{\text{sed}} \quad (28)$$

291 where  $L_s$  is subduction zone length (m),  $S$  is spreading rate ( $\text{m yr}^{-1}$ ) calculated from Ko-  
292 renaga model,  $h_{\text{sed}}$  is thickness of sediments (500 m), and  $\rho_{\text{sed}}$  is sediment density ( $2.5 \text{ g}$   
293  $\text{cm}^{-3}$ ).

294 In addition, shelf sediments have a residence time of 100 Myr, or a rate constant of  
295  $\tau_{\text{scg}} = 1 \times 10^{-8} \text{ yr}^{-1}$ . Shelf sediments are added to the continental crust, representing a  
296 proxy for continental growth by collision and accretion:

$$297 \quad F_{\text{scg},j} = \tau_{\text{scg}} R_j^{\text{shsed}} \quad (29)$$

298 for  $j = \{\text{all species}\}$ .

## 299 **2.7 Crust**

### 300 **2.7.1 Oceanic**

301 Species can enter the oceanic crust through hydrothermal alteration, and the leave  
302 the oceanic crust during subduction. We envision hydrothermal processes essentially as  
303 serpentinization, and overall it adds N to the oceanic lithosphere [Halama *et al.*, 2014].  
304 The amount of hydrothermal alteration is related to both speciation and a volume of hy-  
305 drothermal fluid flow per year:

$$306 \quad F_{\text{hydro},j} = C_j^{\text{deep}} V_{\text{hydro}} H_{\text{eff}} \quad (30)$$

307 for all model species.  $H_{\text{eff}}$  is 1 for K and  $\text{NH}_4^+$ , 0.5 for  $\text{NO}_3^-$  and  $\text{PO}_4^{3-}$ , and 0.01 for Ar.  
308 We set  $V_{\text{hydro}}$  equal to 1.6 Sv [Elderfield and Schultz, 1996; German and Seyfried, 2014]  
309 for nominal runs, but allowed it to vary during sensitivity tests.

310 The subduction flux is calculated by multiplying the mass of crust subducted per  
 311 year by each species concentration in the crust:

$$312 \quad F_{\text{sub},j}^{\text{oc}} = \frac{R_j^{\text{occrust}} O_p}{M_{\text{occrust}}} \quad (31)$$

313 where  $O_p$  is ocean crust produced and  $M_{\text{occrust}}$  is the total mass of crust (g).

314 Thus, the total amount of each species subducted ( $F_{\text{subT}}$ ) is

$$315 \quad F_{\text{subT},j} = F_{\text{sub},j}^{\text{oc}} + F_{\text{sub},j}^{\text{dsed}} + F_{\text{sub},j}^{\text{shsed}} \quad (32)$$

316 Subducted species will either be driven off the slab and sediments or carried beyond  
 317 the subduction barrier and into the mantle. The proportion that is driven off the slab is  
 318 determined by mantle temperature: higher temperature means less material goes into the  
 319 mantle, and lower temperature means more material goes into the mantle. Subducted frac-  
 320 tion is calculated from an average geothermal gradient ( $G_{\text{sub}}$  in  $^{\circ}\text{C km}^{-1}$ ), which in turn is  
 321 calculated from an average mantle temperature ( $T_m$ ):

$$322 \quad G_{\text{sub}} = \frac{12.2(T_m - 273)}{2900} \quad (33)$$

323 where  $T_m$  is in kelvin, 2900 is mantle depth in km, and 12.2 is a conversion factor to ad-  
 324 just average mantle temperature, consistent with the modern average mantle geothermal  
 325 gradient. Subducted fraction is a hyperbolic tangent fit to the data from modern geother-  
 326 mal gradients and subducted fluxes at three modern subduction zones [Elkins *et al.*, 2006;  
 327 Mitchell *et al.*, 2010; Zelenski *et al.*, 2012], and can vary between 0.1 and 1:

$$328 \quad f_{\text{sub}} = 0.5 \left( 1.1 - 0.9 \tanh \left( \frac{G_{\text{sub}} - 6}{0.6} \right) \right) \quad (34)$$

329 The values inside the tanh parenthetical, 6 and 0.6, have units of  $^{\circ}\text{C km}^{-1}$ . We again note  
 330 previous work that has indicated there is likely more complication in the ratio between N  
 331 that is subducted at the trench and that which is sequestered to the mantle. While temper-  
 332 ature is assumed to have a first-order effect in our model, redox [Libourel *et al.*, 2003; Li  
 333 *et al.*, 2016], pH [Mikhail and Sverjensky, 2014], and distribution between fluids and melt  
 334 [Li *et al.*, 2015; Mallik *et al.*, 2018], may all have effects which are not considered here.

335 Thus, the flux of species subducted to the mantle is the product of subducted frac-  
 336 tion, concentration in sediments or crust, and mass of sediments/crust subducted per year:

$$F_{\text{subnet},j} = f_{\text{sub}}F_{\text{subT},j}. \quad (35)$$

for  $j = \{\text{all species}\}$ .

### 2.7.2 Continental

That which is not subducted will either be outgassed at arcs ( $F_{\text{ogarc}}$ ) or be incorporated into the continental crust ( $F_{\text{cg}}$ ). All Ar is outgassed, all K and  $\text{PO}_4^{3-}$  goes into the continental crust. For N,  $f_{\text{Ncgarc}}$  is set to 0.5. That is, half of N released from subducted materials is outgassed at arcs and half is incorporated into the continental crust. This value, 0.5, is an assumption in our model. There is very little data concerning N in subduction zones that is released from the slab. Nitrogen isotopes in granites indicate a biologic source [Boyd, 2001; Johnson and Goldblatt, 2017], which could be from subducted material. More analysis of granitic rocks would help characterize this flux. Thus:

$$F_{\text{cg},j} = (1 - f_{\text{sub}})F_{\text{subT},j} \quad (36)$$

for  $j = \{\text{K}, {}^{40}\text{K}, {}^{40}\text{Ar}, {}^{36}\text{Ar}\}$  and

$$F_{\text{cg},\text{N}} = f_{\text{Ncgarc}}(1 - f_{\text{sub}})F_{\text{subT},\text{N}} \quad (37)$$

for N. All subducted  $\text{PO}_4^{3-}$  is added to the continental crust.

Species in the continental crust have a residence time of 300 Myr, or time constant ( $\tau_w$ ) of  $3.33 \times 10^{-9} \text{ yr}^{-1}$ , which is equivalent to half a Wilson cycle [Nance and Murphy, 2013]. Weathering efficiency depends on atmospheric  $\text{O}_2$ , with weathering increasing with increasing  $\text{O}_2$ :

$$W_{\text{eff},j} = \tau_w \left( a_w + (1 - a_w) \frac{PAL_{\text{O}_2}}{PAL_{\text{O}_2} + k_{\text{weath}}} \right) \quad (38)$$

Where  $a_w$  is the fraction of available material weathered under anoxic conditions (0.1),  $PAL_{\text{O}_2}$  is atmospheric  $\text{O}_2$  compared to present atmospheric levels, and  $k_{\text{weath}}$  is a weathering rate constant ( $1 \times 10^{-3}$ ). Weathered  ${}^{36}\text{Ar}$  and  ${}^{40}\text{Ar}$  are released to the atmosphere, while all other species (N,  $\text{PO}_4^{3-}$ , K) are added to the shelf ocean. As there is no crustal organic

361 material in the model, all continental N is weathered as  $\text{NH}_4^+$ , which is the mineralogically  
 362 most stable form of N. Weathering ( $F_w$ ) is parameterized as:

$$363 \quad F_{w,j} = W_{\text{eff}} R_j^{\text{concrust}} \quad (39)$$

## 364 **2.8 Mantle**

365 Species are added to the mantle at subduction zones ( $F_{\text{subnet}}$ ). It is assumed that  
 366 they instantly homogenize into the mantle (i.e., there are no separate mantle domains).  
 367 Species leave the mantle through degassing at mid-ocean ridges. Degassing is the product  
 368 of the concentration ( $C_j^{\text{man}}$ ) of the species in the mantle and the mass of mantle involved  
 369 in crust genesis ( $M_{\text{melt}}$ ).  $M_{\text{melt}}$  is set to 10 times the mass of oceanic crust produced ( $O_p$ ),  
 370 which and represents generation of crust by 10% partial melt ( $P_m$ ). We assume 90% of  
 371 all species are partitioned to the melt during partial melting ( $K_{\text{dist}}$ ), with 10% remaining  
 372 in the residual. We have chosen this partition of melt to residual to account for the obser-  
 373 vation that mantle rocks that have undergone some melting still have low, but measurable  
 374 N of less than 1 ppm [*Johnson and Goldblatt, 2015*, and references therein]. Thus, mid-  
 375 ocean ridge outgassing is:

$$376 \quad F_{\text{ogmor},j} = C_j^{\text{man}} P_m O_p K_{\text{dist}}. \quad (40)$$

377 We note that there is no explicit treatment of intra-plate, or hot spot, volcanism in  
 378 the model. In addition, we do not distinguish between the upper mantle, transition zone,  
 379 and lower mantle. There are redox changes with depth in the mantle [e.g. *Frost and Mc-*  
 380 *Cammon, 2008*], which have important effects on N solubility in mantle minerals [*Li et al.,*  
 381 *2013, 2016*]. As discussed in *Li et al. [2013]* and *Johnson and Goldblatt [2015]*, the man-  
 382 tle likely has an enormous capacity for N, which likely exceeds its actual content at any  
 383 given time. Future modeling work including mantle structure and redox evolution would  
 384 be an important addition to the work shown herein.

## 385 **2.9 Details on code structure**

386 The model code was constructed to prioritize flexibility. Due to the high number of  
 387 unknowns in the system, giving flexibility was important. We set up the reservoir book-

388 keeping as a structure array in Matlab. This allows for dynamic field names to be used,  
389 which assists in ease of code reading. We also constructed it so that initial conditions are  
390 read in through a separate text file. This allows easy changes, but it is also flexible as not  
391 every species has to be in every box. It also calculates  $^{40}\text{K}$  from K initial conditions, re-  
392 ducing input time and error.

393 The differential equation file is arranged so that it is straightforward to turn vari-  
394 ous fluxes off and on. The purpose for this design is that this model, or one like it, could  
395 be used for not only Earth history, but could be applied to planetary evolution in general.  
396 Different planetary evolution pathways may or may not involve subduction, different at-  
397 mospheric compositions, or differing biologic pathways and metabolisms. Testing the re-  
398 sponse of the system to such differences, perturbations, and the presence or absence of  
399 one or more fluxes could be of great value in studying planetary evolution.

400 In detail, we used Matlab's ode15s solver. This is a variable-step, variable-order  
401 solver that uses numerical differentiation formulas of orders 1 to 5. We set the relative  
402 error tolerance to  $1 \times 10^{-7}$  and a maximum step size of  $10^6$  years. Code is available in the  
403 supplementary material. Please contact us if you wish to use this code in order to obtain  
404 the latest version.

### 405 **3 Results and Discussion**

406 We ran the model in all runs for 4.5 Ga, after a spin up period of 10 Myr to equili-  
407 brate atmosphere, ocean, and sediment boxes. All biologic N fluxes are "available" at each  
408 model step.

#### 409 **3.1 Nominal Run**

410 In order to test the effects of different conditions over Earth history, such as oxy-  
411 genic photosynthesis evolution time and style of mantle cooling, we first describe the re-  
412 sults of a nominal model run.

413 This realization is based on a conservative set of assumptions regarding initial and  
414 boundary conditions and choice of parameterizations (Fig. 3). Mantle cooling and mid-  
415 ocean ridge crust production (i.e., mid-ocean ridge outgassing) is from *Korenaga* [2010],  
416 with the fraction of subducted N retained to the deep mantle dependent on mantle temper-  
417 ature. The atmospheric  $\text{O}_2$  history is prescribed, and oxygenic photosynthesis evolves at

418 2.8 Ga. Plate tectonics starts at 3.5 Ga, continental weathering timescale is 300 Myr, and  
 419 hydrothermal alteration is parameterized as a fixed volume flow (1.6 Sv).

420 We estimate the proportions of N that start in the atmosphere and the mantle at the  
 421 end of the magma ocean phase of Earth history, and use this as the initial condition for  
 422 the nominal run (Appendix B: ). Using results from *Libourel et al.* [2003], which relates  
 423  $pN_2$  to N dissolved in basaltic magma, and a mantle  $fO_2$  of IW-2 [*Wood et al.*, 2006],  
 424 which is expected at the end of core formation, we calculate  $N_2$  concentration in a magma  
 425 ocean for a range of atmospheric  $pN_2$  values. We assume the entire mantle experienced  
 426 a magma ocean phase. Then, given this relationship, we can estimate a total N budget  
 427 and what proportion of that N starts in the atmosphere and the mantle. We select a total  
 428 N budget for the nominal run to be consistent with budget estimates from *Johnson and*  
 429 *Goldblatt* [2015], and one that reproduces the current distribution of N in the atmosphere  
 430 (1 PAN) and the mantle (>3 PAN). Our starting conditions are therefore total N of 4.8  
 431 PAN, with 80% starting in the atmosphere and 20% in the mantle. The evolution of major  
 432 N reservoirs (atmosphere, mantle, continental crust, ocean sediments) is shown in Fig. 4  
 433 with atmosphere-ocean gases and nutrients shown in Fig. 5.

Table 4: Nitrogen reservoir and flux comparisons: nominal model output results compared to literature N mass estimates from *Johnson and Goldblatt* [2015], with continental crust from *Johnson and Goldblatt* [2017]. Reservoirs are in units of  $10^{18}$  kg N, while ocean concentrations are shown in  $\mu\text{M}$ . Shallow ocean model results are the average of low-latitude, high-latitude, and shelf boxes. Deep ocean values from the literature are for 1000 m depths. Model values are from the end of nominal model run (i.e., modern values). Fluxes are in  $\text{Tmol N yr}^{-1}$  unless otherwise noted. Model results are shown for modern day reservoir fluxes.

Reservoir/Flux	Model	Literature	Reference
Atmosphere	3.92	4	<i>Johnson and Goldblatt</i> [2015]
Mantle	12	$24 \pm 16$	<i>Johnson and Goldblatt</i> [2015]
Continental Crust	1.8	$1.7 - 2.7$	<i>Johnson and Goldblatt</i> [2015, 2017]
Oceanic Lithosphere	0.05	$0.2 \pm 0.02$	<i>Johnson and Goldblatt</i> [2015]
Total ocean Sediments	1.2	$0.41 \pm 0.2$	<i>Johnson and Goldblatt</i> [2015]
Shallow ocean $\text{NO}_3^-$	22	7	<i>Gruber</i> [2008]

*Continued on next page*

**Table 4 Reservoir comparison – continued from previous page**

Reservoir/Flux	Model	Literature	Reference
Deep ocean NO <sub>3</sub> <sup>-</sup>	25	31	<i>Gruber</i> [2008]
Shallow ocean NH <sub>4</sub> <sup>+</sup>	2.4	0.3	<i>Gruber</i> [2008]
Deep ocean NH <sub>4</sub> <sup>+</sup>	1.5	0.01	<i>Gruber</i> [2008]
Shallow ocean PO <sub>4</sub> <sup>3-</sup>	0.12	< 1	<i>Garcia et al.</i> [2014]
Deep ocean PO <sub>4</sub> <sup>3-</sup>	0.36	1 – 3	<i>Garcia et al.</i> [2014]
Shallow ocean O <sub>2</sub>	533	220 – 400	<i>Garcia et al.</i> [2014]
Deep ocean O <sub>2</sub>	530	40 – 400	<i>Garcia et al.</i> [2014]
<i>Biologic fluxes</i>			
N-fixing	6.4	13	<i>Gruber and Galloway</i> [2008]; <i>Vitousek et al.</i> [2013]
Nitrification	19	85	<i>Gruber</i> [2008]
Denitrification	6	22	<i>Gruber</i> [2008]
N-remineralization	21	93	<i>Gruber</i> [2008]
<i>Geologic Fluxes</i>			
Continental weathering	0.43	1.1	<i>Houlton et al.</i> [2018]
Burial/sedimentation	0.73	0.07	<i>Gruber</i> [2008]
Total subduction	0.66	0.0064	<i>Mallik et al.</i> [2018]
		0.0094	<i>Busigny et al.</i> [2011]
		0.1	<i>Halama et al.</i> [2014]
Arc outgassing	0.08	0.0375	<i>Catling and Kasting</i> [2017]
Mid-ocean ridge outgassing	0.2	0.0038	<i>Catling and Kasting</i> [2017]
Total outgassing	0.28	0.09	<i>Catling and Kasting</i> [2017]

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We focus first on model output at the modern day. The nominal run reproduces the modern atmospheric and estimated mantle N masses well. The mantle value, specifically, is somewhat lower, but within the estimated mantle N budget from *Johnson and Goldblatt* [2015], which is  $7 \pm 4$  PAN. The nominal run has 3.25 PAN in the mantle at modern. We present full comparisons with values from the literature in Table 4.

440 Model output is consistent with estimates for the modern day N budget in deep sed-  
441 iments of  $\sim 0.1$  PAN [Johnson and Goldblatt, 2015], and continental crust. For example,  
442 recent work using glacial tills as a proxy for upper continental crust through time sug-  
443 gest a secular increase in crustal N during the Precambrian [Johnson and Goldblatt, 2017].  
444 The authors suggest that isotopic evidence is most consistent with this addition of N to  
445 the continents being biological in origin. Atmospheric N is biologically fixed and then  
446 subsequently added to the continents either via collision of marginal marine sediments or  
447 incorporation from subduction zone processing, with a total crust N content of 0.5-0.67  
448 PAN. While we do have both of these fluxes in our model, they are only very general. It  
449 is well known that the Earth has gone through periods of orogenic activity and periods of  
450 quiescence [e.g., Condie, 2013] with variable passive margin extent [Bradley, 2008], and  
451 these variations are not captured in our model.

452 In all model runs, prior to the evolution of oxygenic photosynthesis the N cycle is  
453 marked by mantle degassing and atmospheric N growth, after a period of atmospheric  
454 equilibration with oceanic sediments. (Figs. 4 - 6). High mantle temperatures, combined  
455 with low efficiency export production and N-fixing results in net mantle outgassing and  
456 atmospheric growth for the first 1.5 Ga of model output. Biologic N fluxes (Fig. 7) are  
457 low prior to oxygenic photosynthesis, due to lower overall productivity and burial. Then,  
458 coincident with, and caused by, the appearance of oxygenic photosynthesis, the atmosphere  
459 is drawn down, with an increase in all the geologic N reservoirs. Deep ocean sediments  
460 increase most quickly, with continental crust and the mantle increasing more slowly. At  
461 the GOE, an increase in weathering drives a spike in productivity and further atmospheric  
462 draw-down due to enhanced N-fixing. The Lomagundi-Jatuli type event, with high pro-  
463 ductivity, lasts for  $\sim 50$  Myr. At about 1.6 Ga, the mantle and atmosphere have equal N  
464 budgets, and the mantle continues to increase at the expense of all other reservoirs until  
465 the present day.

466 While the nominal run reproduces modern N distribution well, there are discrepan-  
467 cies between modeled biologic and geologic fluxes and estimates of these fluxes from the  
468 literature (Fig. 4). The model somewhat underestimates N-fixing, nitrification, and denitri-  
469 fication. It is possible to explain some of this discrepancy by the lack of continental bio-  
470 logic N-cycling in our model, since at present continental ecosystems account for half of  
471 global biologic N cycling [e.g., Gruber and Galloway, 2008]. Similarly, nominal output for

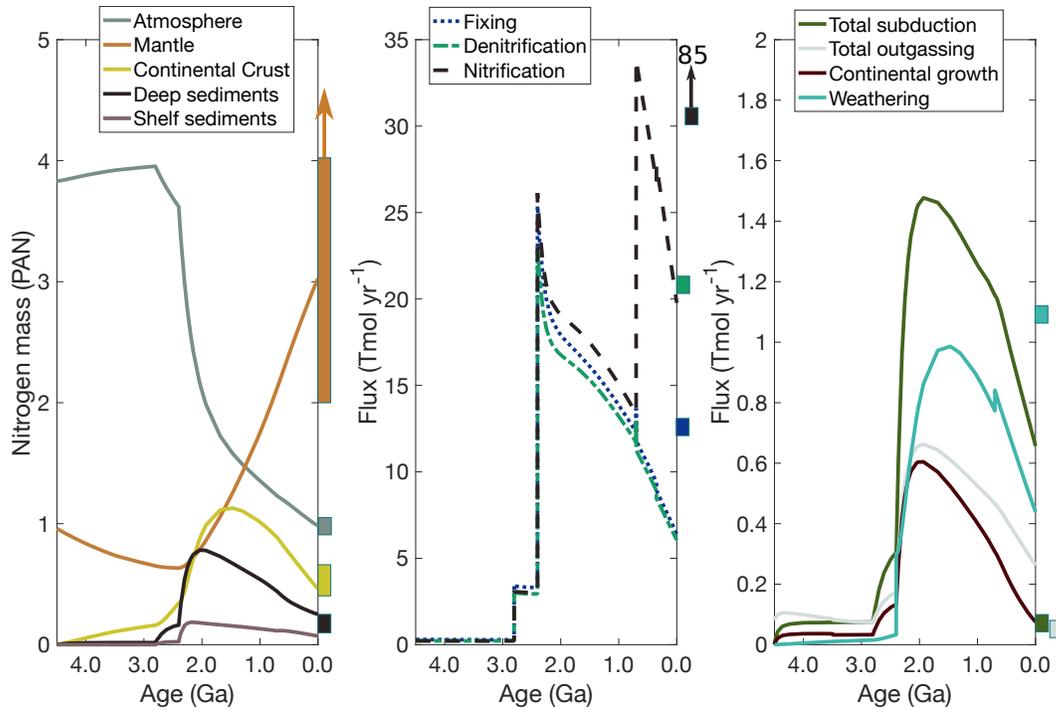


Figure 4: a. Nitrogen reservoirs through time from a nominal run. b. Biologic nitrogen fluxes and c. Geologic fluxes. Estimates for modern amounts are shown as colored bars next to each panel [Gruber, 2008; Gruber and Galloway, 2008; Busigny et al., 2011; Vitousek et al., 2013; Halama et al., 2014; Johnson and Goldblatt, 2015; Catling and Kasting, 2017; Mallik et al., 2018; Houlton et al., 2018].

472 continental N weathering is less than a recent study [Houlton et al., 2018]. Adding more  
 473 explicit treatment of continental N cycling would be a welcome addition to this model.

474 For the other major geologic fluxes, outgassing and subduction, the EarthN model  
 475 output is higher than estimates from the literature. This indicates that either subduction  
 476 of N is not as efficient as we describe, and recycling into the mantle is less, or literature  
 477 estimates of subduction and outgassing are too low. It is notoriously difficult to estimate  
 478 N fluxes outgassing at subduction zones and mid-ocean ridges [Fischer et al., 2002; Elkins  
 479 et al., 2006], due to high background atmospheric N<sub>2</sub>. In addition, there are very few esti-  
 480 mates of N cycling in subduction zones [Fischer et al., 2002; Elkins et al., 2006; Mitchell  
 481 et al., 2010; Halama et al., 2014; Mallik et al., 2018], and it is possible that this flux is  
 482 being underestimated in the literature due to the difficulty in analyzing silicate-bound N.

### 3.1.1 Ocean nutrients through time

Our results yield several important predictions of nutrient content of the ocean through time. First, and unsurprisingly,  $\text{NH}_4^+$  is the dominant bioavailable N species in the ocean, and  $\text{PO}_4^{3-}$  remains high ( $\sim 1 - 3 \mu\text{M}$ ) before oxygenic photosynthesis. Second, after the appearance of oxygenic photosynthesis and the associated increase in productivity (Fig. 3), burial increases. The increase in burial is reflected in the increase in N in ocean sediments and in all biologic N fluxes (Fig. 4). We note here that since we do not include abiotic N-fixing, and instead assume biologic N-fixing could operate throughout the model run, we might be slightly overestimating early Archean N-fixing if biologic fixing did not evolve till 3.2 Ga [Stüeken *et al.*, 2015]. For example, Navarro-González *et al.* [2001] suggests  $2.1 \times 10^{10} \text{ mol yr}^{-1}$  could be fixed abiotically by lightning, while the minimum N-fixing we calculate is  $2.9 \times 10^{11} \text{ mol yr}^{-1}$ . At the same time as the increase in N-cycle fluxes,  $\text{PO}_4^{3-}$  concentrations drop an order of magnitude, again the result of increased productivity and burial. We also note that there is a small oxygen oasis in the shelf ocean box, which is consistent with evidence for localized oxic conditions prior to widespread oxygenation at the GOE [Anbar *et al.*, 2007] Additionally, nutrient concentrations increase after the GOE, as the result of increased weathering efficiency.

Third,  $\text{NH}_4^+$  and  $\text{NO}_3^-$  are at about the same concentration in the Proterozoic. This balance is the result of  $\text{O}_2$  levels, and so is dependent on our  $\text{O}_2$  forcing scheme, which sets Proterozoic  $\text{O}_2$  levels at 1% of modern. There is not agreement on the exact level of  $\text{O}_2$  in the Proterozoic [Lyons *et al.*, 2014; Planavsky *et al.*, 2014; Reinhard *et al.*, 2016; Zhang *et al.*, 2016], but generally the maximum estimates are no greater than 10% of modern. Thus, the transition to a  $\text{NO}_3^-$ -rich ocean is predicted to only occur at the NOE, and our modeling does not indicate any sort of N-limitation during the Proterozoic. We do not, however, model a specific increase in productivity due to the evolution of eukaryotes, which might be expected to enhance biologic N-cycling [e.g., Zerkle and Mikhail, 2017, and references therein].

### 3.1.2 Different plate tectonic histories

Different mantle cooling history could have a large effect on the transfer and sequestration of N from the surface into the mantle over time. For example, if mantle temperatures were hotter in the Archean, one might expect both faster mantle convection and less

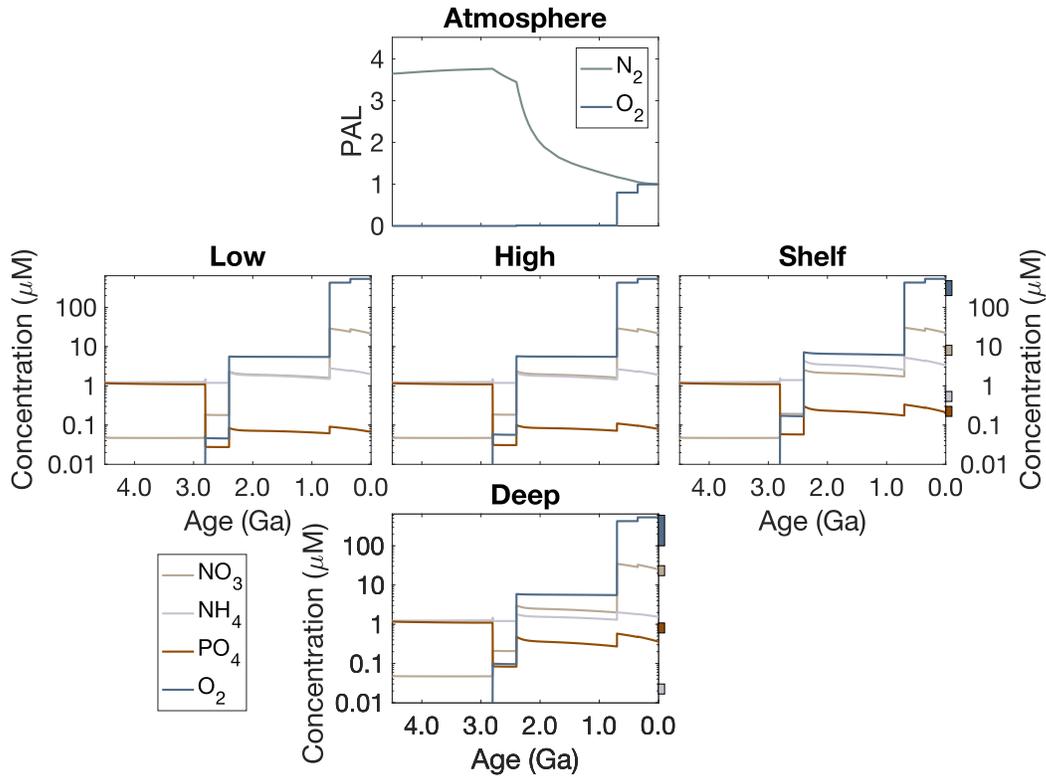


Figure 5: Nitrogen,  $O_2$ , and  $PO_4^{3-}$  surface reservoirs through time for a nominal run.  $NH_4^+$  is the dominant N species until the Neoproterozoic Oxygen Event, and  $PO_4^{3-}$  is high until the evolution of oxygenic photosynthesis. A small  $O_2$  oasis exists in the late Archean shelf ocean. Literature estimates for modern values are shown as colored bars next to shallow boxes; the shallow ocean bars are for the average shallow ocean, and deep ocean represents 1000 m depth [Gruber, 2008; Garcia et al., 2014].

514 efficient retention of N at subduction zones. Relatedly, if mantle temperature is not the  
 515 main control on N retention into the mantle at subduction zones, different subduction effi-  
 516 ciencies would lead to correspondingly different N histories.

517 To test these possibilities, we ran the model with three different styles of mantle  
 518 cooling/plate tectonic transfer of N from the surface to the mantle (Fig. 6). The first, as  
 519 described in the nominal run section, is based on Korenaga [2010]. In the second, mantle  
 520 temperature, ocean crust production, and subducted crust are all constant, set to the aver-  
 521 age of each value from Sandu et al. [2011], which uses a “canonical” mantle cooling. In

522 addition, the fraction of subducted N that is transported to the deep mantle is held con-  
523 stant at 0.2. In the third realization, we allow subducted fraction to vary with canonical  
524 mantle evolution temperature.

525 In all three realizations, prior to oxygenic photosynthesis, there is net mantle out-  
526 gassing and atmospheric growth. Similarly, after oxygenic photosynthesis and more effi-  
527 cient export production, there is net atmospheric drawdown into geologic reservoirs. The  
528 amount of drawdown by subduction with canonical mantle cooling, with either constant  
529 or temperature-linked efficiency, is more overall than in the nominal run, up to 4 PAN in  
530 the latter. Constant subduction efficiency, however, cannot sequester enough atmospheric  
531 N into the mantle to result in a 1 PAN atmosphere at modern. In addition, this run results  
532 in more N in the atmosphere than the mantle, contradicting estimates of N distribution on  
533 Earth today [Johnson and Goldblatt, 2015]. Interestingly, the overall pattern is insensitive  
534 to mantle cooling history.

535 We also explored realizations where the time of plate tectonic initiation and oxy-  
536 genic photosynthesis were varied (Fig. 7). The initiation of plate tectonics does not af-  
537 fect the overall pattern, nor does it greatly effect the distribution of N between various  
538 reservoirs. Mantle cooling, and its effect on subduction efficiency, has a larger effect than  
539 timing of plate initiation alone. Similarly, only when biologic productivity increases after  
540 oxygenic photosynthesis do major changes in N distribution occur.

### 541 ***3.1.3 Different oxygenic photosynthesis appearance***

542 Another main “knob” on the control panel of the N cycle is how biologic activ-  
543 ity processes this in the oceans. As seen in the nominal run, the appearance of oxygenic  
544 photosynthesis and the GOE exert a large control over how active N-fixing, nitrification,  
545 and denitrification are. To test for any effects of different times of oxygenic photosynthe-  
546 sis evolution (Fig. (Fig. 7), we ran the model with standard conditions, but altered when  
547 oxygenic photosynthesis evolves: early (3.5 Ga), middle (2.8 Ga, standard), and late (2.4  
548 Ga). These times were chosen to coincide with early fossil evidence for photosynthetic life  
549 [Hofmann *et al.*, 1999], molecular and geochemical evidence for oxygenic photosynthesis  
550 by 2.8 Ga [see Buick, 2008], and the GOE at 2.4 Ga [Farquhar *et al.*, 2000].

551 In all runs, when oxygenic photosynthesis evolves, atmospheric N is drawn down.  
552 Initially, N is sequestered into deep sediments, then, if plate tectonics is operating, sent

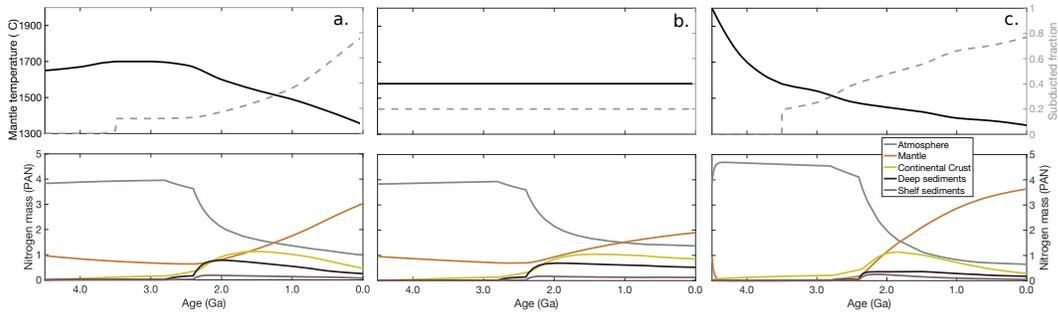


Figure 6: Nitrogen reservoirs and subducted fraction for different subduction parameters. a.) nominal run, b.) constant subduction, c.) canonical subduction. The Archean in all cases is characterized by net mantle outgassing, but outgassing is rapid in canonical subduction runs. Net drawdown occurs after oxygenic photosynthesis evolves, and deep sediments and continental crust increases as well.

553 into the mantle and continental crust. If oxygenic photosynthesis appears later, atmo-  
 554 spheric N reservoir reaches a slightly higher maximum prior to drawdown. In addition,  
 555 all else being equal, a later appearance of oxygenic photosynthesis results in a slightly  
 556 higher  $pN_2$  at modern. Overall, the main change in N-history occurs at the GOE, driven  
 557 by increased weathering, nutrient supply, and enhanced biologic productivity.

### 558 3.2 Atmospheric $pN_2$ comparison with other reconstructions

559 As mentioned in the introduction, there is a discord between modern geochemi-  
 560 cal data suggesting net ingassing of the atmosphere through time [Busigny *et al.*, 2011;  
 561 Nishizawa *et al.*, 2007; Barry and Hilton, 2016] and either net outgassing [Som *et al.*, 2012,  
 562 2016] or atmospheric stability since the Archean [Marty *et al.*, 2013]. Our model strongly  
 563 suggests dynamic behavior over time, with the N distribution on Earth responding to changes  
 564 in biologic and geologic evolution over time.

565 In order to match constraints for similar or lower atmospheric N mass in the past  
 566 [Marty *et al.*, 2013; Som *et al.*, 2012, 2016], but still end up with a 1 PAN modern atmo-  
 567 sphere, our model has to be tuned to very specific parameters (Fig. 8) within an otherwise  
 568 nominal run. Given our standard total N budget (4.8 PAN), the mantle must start with the  
 569 majority (90%) of total N, due to net outgassing during the Hadean and Archean. In addi-  
 570 tion, the net subduction of N at subduction zones has to be low and constant (10%), as an

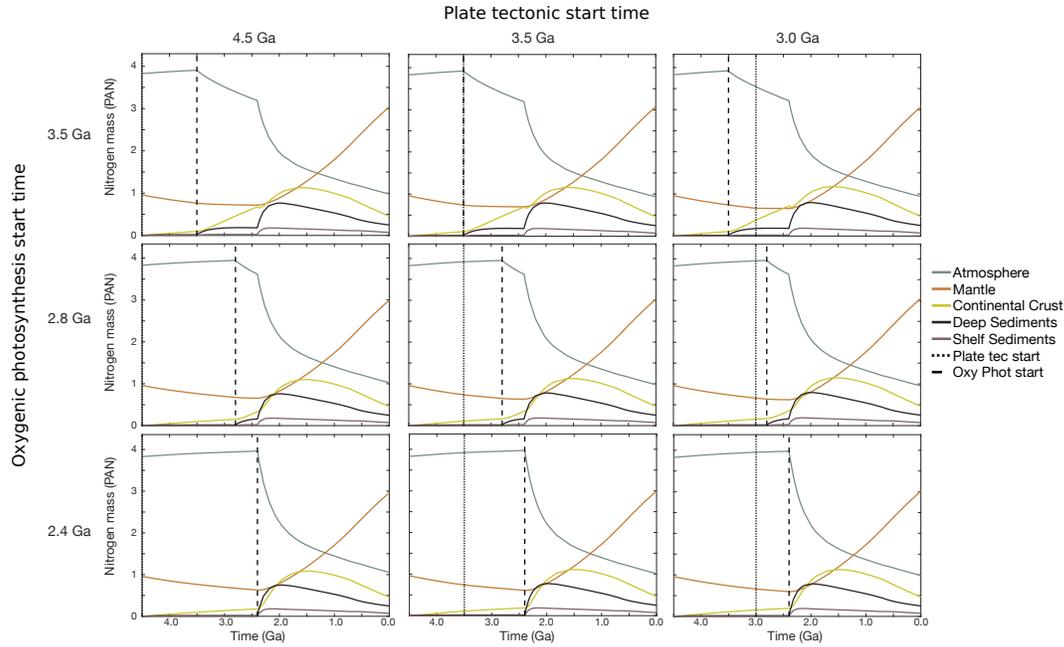


Figure 7: Nominal runs varying plate tectonic (4.5, 3.5, 3.0 Ga) and oxygenic photosynthesis starting time (3.5, 2.8, 2.4 Ga). The overall pattern for major N reservoirs is similar for all cases. Mantle N increases when subduction begins, atmospheric drawdown of N into ocean sediments occurs when oxygenic photosynthesis evolves, and further drawdown occurs after the GOE.

571 increase in net subduction over time results in atmospheric drawdown in all model runs.  
 572 We also have to increase hydrothermal circulation from 5 to 50 Sv, which limits  $\text{PO}_4^{3-}$  and  
 573 in turn limits atmospheric drawdown via N-fixing. The model with these parameters can  
 574 reproduce the constraints of 1 PAN at 3.46 Ga [Marty *et al.*, 2013] and a 0.5 PAN atmo-  
 575 sphere at 2.7 Ga [Som *et al.*, 2012, 2016] but still result in a 1 PAN modern atmosphere.  
 576 Even in this case, there is still a 1.75 PAN atmosphere at 2.8 Ga, when oxygenic photo-  
 577 synthesis evolves. The atmosphere undergoes a dynamic evolution.

578 Lower atmospheric mass in the past cannot be specifically ruled out by our model  
 579 output, but such lower mass would present a number of interesting implications. The lack  
 580 of evidence for large glaciations in the Archean is difficult to reconcile with low atmo-  
 581 spheric mass [Goldblatt *et al.*, 2009]. Similarly, the majority of the Proterozoic, or “boring  
 582 billion”, lacks evidence for glaciation, implying warm climate. If the Earth had less than a  
 583 one PAN atmosphere, there would need to be  $10^{-2.2}$  bars of  $\text{CO}_2$ , and even more with less  
 584 N.

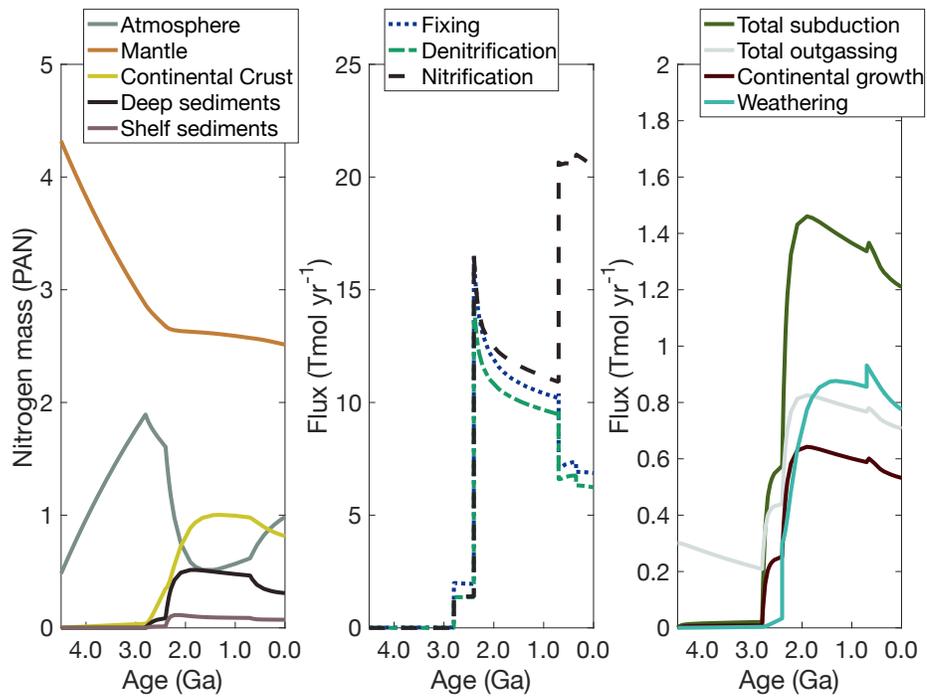


Figure 8: Nominal run but with low starting atmospheric mass, 5% starting N in the atmosphere, constant net subduction (10%), and high (50 Sv) hydrothermal circulation. These conditions lead to a model realization consistent with previous estimates of a 1 PAN atmosphere at 3.46 Ga [Marty *et al.*, 2013] and 0.5 PAN at 2.7 Ga [Som *et al.*, 2012, 2016].

### 3.3 Investigating unknown nitrogen distribution: Monte Carlo simulations

Despite recent interest in geologic and Earth system N cycling [Johnson and Goldblatt, 2015; Zerkle and Mikhail, 2017; Johnson and Goldblatt, 2017], there is not a consensus on how much N the Earth contains and how it has moved between different reservoirs over time. In addition, and especially in the Hadean and Archean, a number of parameters that could affect the N cycle are not well constrained. These include when oxygenic photosynthesis first appeared, the rate of hydrothermal alteration of ocean crust, deep water upwelling, continental weathering, and the initiation of plate tectonics [Van Hunen and Moyen, 2012]. To investigate how changing these poorly constrained parameters may have affected the N cycle over time, we ran Monte Carlo simulations (n=1000) where a number of parameters were given random values within a prescribed range (Table 5, Figs. 9-10).

Table 5: Range of values used for Monte Carlo simulations. PAN is Present Atmospheric Nitrogen, or  $4 \times 10^{18}$  kg

Parameter	Range (units)
Upwelling	0.16–16 Sv
Oxygenic photosynthesis start time	2.4-3 Ga
Plate tectonics start time	3-4 Ga
Weathering timescale	50-500 Myr
Hydrothermal flow rate	$0.5-50 \times 10^{16}$ L yr <sup>-1</sup>
Total N	2-12 PAN
Percent starting in atmosphere	0-100%

Strikingly, our model suggests that the amount of N found in the atmosphere today may in some part be related to the total N in the planet (Fig. 9). There is a strong correlation between the total N in the model and the atmospheric N mass after 4.5 Gyr of planetary evolution. Monte Carlo results that have 1 PAN atmosphere at the present day are those with a total N budget of  $\sim 4 - 6$  PAN, similar to independent budget estimates [Johnson and Goldblatt, 2015]. On Earth, the atmospheric N content directly relates to the total planetary N budget. It is possible that this proxy may work for other terrestrial plan-

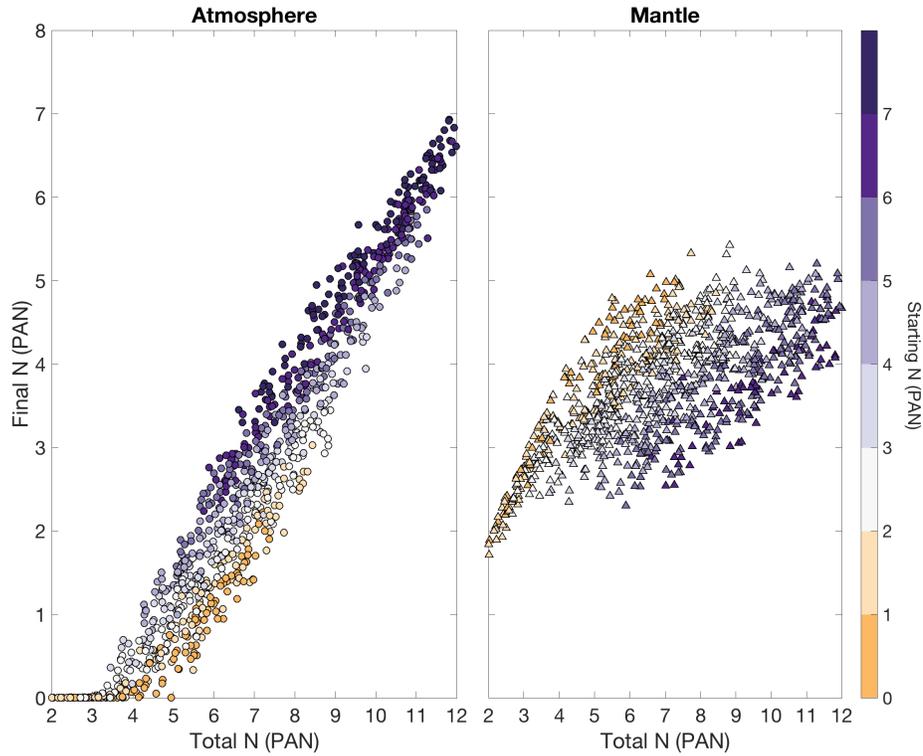


Figure 9: Final atmospheric and mantle N vs total N for 1000 Monte Carlo simulations. Note strong correlation between atmospheric N and total N, and that for very low N budgets, the atmospheric mass is small. Runs that results in a 1 PAN atmosphere have 5 PAN total N. The mantle saturates at 3 PAN.

604 ets, given evidence for plate tectonics (e.g., linear mountain belts, bimodal topographies)  
 605 and biologic N cycling (e.g.,  $N_2$  and  $O_2$  coexisting,  $N_2O$ ), atmospheric N could serve as  
 606 an estimate for total planetary N content.

607 The mantle N content also increases with increasing total content, but tends to “sat-  
 608 urate” at 4.5 PAN (Fig. 10). This is because net subduction and outgassing at mid-ocean  
 609 ridges tend to balance each other, while N-fixing is limited by  $PO_4^{3-}$  availability. That is,  
 610 the rate at which organisms can fix N is not enough to outpace overall outgassing, thus at  
 611 higher total N budgets, N accumulates in the atmosphere. For very small total N budgets  
 612 less than 3 PAN, N-fixing is efficient enough to draw down the atmosphere almost com-  
 613 pletely into the mantle.

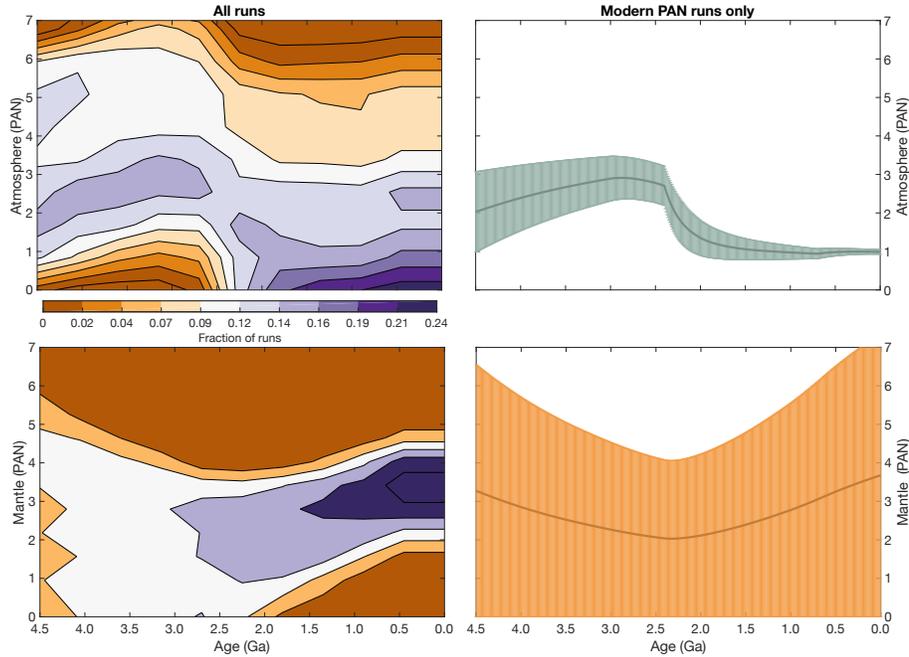


Figure 10: Results of Monte Carlo runs for atmosphere and mantle values through time for all runs (a-b) and just runs that result in a 1 PAN present atmosphere (c-d). Panels c-d show the mean and one standard deviation. The mantle tends to evolve towards a final value of between 3-4 over time, while the atmosphere is more variable. Most runs end with a 2 PAN atmosphere at modern and throughout much of the Proterozoic and Archean, with two other nodes at 0.5 and 4 PAN. Runs that result in a 1 PAN atmosphere start with a  $\sim 2$  PAN atmosphere at 4.5 Ga., and are drawn down in the late Archean. Mantle N for runs that result in a 1 PAN atmosphere average 4 PAN, but are variable.

614 In addition, the EarthN model does not thoroughly parameterize mantle evolution  
 615 over time. Thus, we predict that model output suggesting mantle saturation at 4.5 is a  
 616 minimum estimate of the true N content of the mantle.. Previous work has estimated that  
 617 the mantle has an enormous capacity for N, and could possibly contain many 10s of PAN  
 618 [Li *et al.*, 2013; Smith *et al.*, 2014; Johnson and Goldblatt, 2015].

619 Monte Carlo realizations that result in a 1 PAN present atmosphere show the same  
 620 overall pattern as the nominal run (Fig. 10). On average, the atmosphere starts out with  
 621 greater than modern mass, then decreases, again likely due to the evolution of oxygenic  
 622 photosynthesis, in the late Archean. The atmosphere remains at approximately 1 PAN

623 throughout the Proterozoic, with a small increase at the NOE, due to enhanced denitrifi-  
624 cation at this time. Even when we allow for a random total N and a random amount of N  
625 starting in the atmosphere, the overall trend in the atmospheric evolution is to be drawn  
626 down from higher Archean values towards the modern. In contrast, the mantle stays con-  
627 sistent on average, at its saturation of about 4 PAN. The standard deviation shown in Fig.  
628 10-d indicates there are many mantle N paths which are consistent with the EarthN model  
629 evolving a 1 PAN present atmosphere.

630 As previously mentioned, the temperature history of the mantle, and behavior of N  
631 in different geothermal regimes exerts a strong control on the evolution of N in the Earth  
632 system over time. This behavior also depends on how much temperature actually controls  
633 N volatilization at subduction zones. Studies have shown that redox [Li *et al.*, 2013], tem-  
634 perature/pressure [Li and Keppeler, 2014], distribution of N between fluid and melt [Mallik  
635 *et al.*, 2018], and pH [Mikhail and Sverjensky, 2014] also exert control over N speciation  
636 and retention in the mantle. The interaction of these different factors in geologic evolution  
637 could have had a large effect on N cycling over Earth history [Mikhail and Howell, 2016].  
638 We predict that redox evolution is likely to have the largest effect on N processing and  
639 storage in the mantle. The upper mantle and mantle lithosphere have, on average, been at  
640 their current redox state since 3.5 Ga [Canil, 2002]. Arc basalts, however, are more ox-  
641 idized than MORBs with otherwise similar chemical composition [Kelley and Cottrell,  
642 2012; Brounce *et al.*, 2014]. In addition, the deeper mantle is more reducing than the up-  
643 per mantle [Frost and McCammon, 2008].

644 It follows, then, that N is more soluble in the reduced lower mantle than the more  
645 oxidized upper mantle and subduction zone mantle wedge. As the mantle has become  
646 more oxidized through time, N recycling to the atmosphere would be favored. If the ox-  
647 idation state of subduction zone mantle has similarly increased through time, this would  
648 enhance recycling of N to the surface [e.g., Mikhail and Sverjensky, 2014]. Thus, there  
649 are competing features controlling N recycling into the mantle: decreasing temperature  
650 and increasing  $fO_2$ . Given observations of net N retention at modern subduction zones  
651 [Li *et al.*, 2007; Mitchell *et al.*, 2010; Halama *et al.*, 2014], we hypothesize that mantle  
652 wedge temperature is the dominant control of N recycling efficiency, at least on the mod-  
653 ern Earth. How this balance of redox and temperature has controlled N, and other volatile,  
654 recycling over Earth history has important implications for the evolution of the surface and  
655 interior of the planet.

656 The above discussion highlights a broader point regarding model construction. Herein,  
657 we have constructed an Earth system N cycle model, and presented a nominal run based  
658 on plausible assumptions about the Earth through time. The results presented, however,  
659 should not be taken as gospel, dogma, or actuality. There are a number of fluxes and fac-  
660 tors in the Earth which could affect results of the EarthN model. In addition to mantle  
661 chemistry, mantle capacity for N is enormous [Li *et al.*, 2013], and the great potential size  
662 of this reservoir could have major influence over N cycling during Earth history. The lack  
663 of continental ecosystems, and simple treatment of hydrothermal activity in oceanic crust  
664 in this model could be important parameters to investigate. The addition of isotopes to the  
665 model would allow for predictions that could be tested in the rock record. We envision fu-  
666 ture studies to explore this wider parameter space, both for specific intervals in time and  
667 for grand trends over Earth history.

#### 668 **4 Conclusions**

669 We have constructed an Earth system N model, EarthN, that includes biologic and  
670 geologic fluxes to predict the distribution of N in the major reservoirs of the Earth through  
671 time. In addition to linking the N cycle to  $\text{PO}_4^{3-}$  availability, the model is driven by chang-  
672 ing  $\text{O}_2$  abundance and mantle cooling with plate tectonics. Model output is consistent  
673 with movement of N between the three major reservoirs (atmosphere, mantle, continen-  
674 tal crust) in significant amounts over Earth history.

675 In all model runs, the early part of Earth history, from 4.5-2.8 Ga, is characterized  
676 by net mantle outgassing and atmospheric growth. This early history is due to high man-  
677 tle temperatures and inefficient export production. After the evolution of oxygenic photo-  
678 synthesis, atmospheric N is immediately drawn down and sequestered in sediments due  
679 to increased export production. At the Great Oxidation Event, increased weathering and  
680 nutrient delivery enhances export production, which in turn enhances atmospheric draw-  
681 down via N-fixation. Mantle cooling over time, with associated increase in efficiency of N  
682 subduction, facilitates biologically fixed N to be sequestered into geologic reservoirs over  
683 time.

684 One of the strongest controls on the atmospheric mass of N through time, and espe-  
685 cially the modern mass of the atmosphere, is the total N in the Bulk Silicate Earth. Monte  
686 Carlo simulations that vary a number of parameters (deep water upwelling, hydrothermal

687 circulation, oxygenic photosynthesis appearance, weathering timescale, total N and distri-  
688 bution) that result in a 1 PAN atmosphere after 4.5 Ga of model evolution are most con-  
689 sistent with a total BSE N budget of  $\sim 4 - 6$  PAN. The mantle tends to saturate at 4-4.75  
690 PAN. The mantle is the dominant N carrier for total N budgets below 6-7 PAN, while the  
691 atmosphere is dominant at higher values.

692 The EarthN model shows that the distribution of N in the Earth system through time  
693 could have varied significantly. Nominal model runs result in net atmospheric drawdown  
694 over time, which is consistent with geochemical proxies. There are a number of controls  
695 on N history, including appearance of oxygenic photosynthesis, mantle cooling, and N in  
696 subduction zones. We anticipate further work in this area to focus on how temperature  
697 and redox control N at subduction zones. Equally, the cycling of N in the mantle over  
698 time is poorly known but crucially important. There is potential for not only investigating  
699 Earth history, but exploration of Venus, Mars, and potential exoplanetary targets in the  
700 future.

## 701 **Acknowledgments**

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706 Supporting model code and output data can be found as a supplemental file with  
707 this manuscript. In addition, code will be available at the corresponding author's webpage:  
708 [www.benwjohnson.com](http://www.benwjohnson.com).

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711

## 712 **A: Differential equations**

713 Based on the above model description, we write a series of differential equations to  
714 solve for model species in boxes.

715 **Atmosphere**

$$716 \quad \frac{dR_j^{\text{atm}}}{dt} = \sum_{i^*} F_{\text{as},j}^{\text{atm}-i^*} + F_{\text{ogarc},j} \quad (\text{A.1})$$

717 for  $j = \{\text{N}_2, {}^{40}\text{Ar}, {}^{36}\text{Ar}\}$  and  $i^*$  includes air-sea flux from all shallow ocean boxes ({low,  
718 high, shelf}).

719 **Low- and high-latitude shallow ocean**

$$720 \quad \frac{dR_{40\text{Ar}}^i}{dt} = F_{\text{mix},40\text{Ar}}^i + F_{\text{rd}}^i - F_{\text{as},40\text{Ar}}^{\text{atm}-i} \quad (\text{A.2})$$

$$721 \quad \frac{dR_{36\text{Ar}}^i}{dt} = F_{\text{mix},36\text{Ar}}^i - F_{\text{as},36\text{Ar}}^{\text{atm}-i} \quad (\text{A.3})$$

$$722 \quad \frac{dR_{40\text{K}}^i}{dt} = F_{\text{mix},40\text{K}}^i - F_{\text{rd}}^i \quad (\text{A.4})$$

$$723 \quad \frac{dR_{\text{K}}^i}{dt} = F_{\text{mix},\text{K}}^i \quad (\text{A.5})$$

$$724 \quad \frac{dR_{\text{PO4}}^i}{dt} = F_{\text{mix},\text{PO4}}^i - F_{\text{EXT}}^i \quad (\text{A.6})$$

$$725 \quad \frac{dR_{\text{NO3}}^i}{dt} = F_{\text{mix},\text{NO3}}^i - F_{\text{out},\text{NO3}}^i + F_{\text{nit}}^i - F_{\text{den}}^i \quad (\text{A.7})$$

$$726 \quad \frac{dR_{\text{NH4}}^i}{dt} = F_{\text{mix},\text{NH4}}^i - F_{\text{out},\text{NH4}}^i - F_{\text{nit}}^i \quad (\text{A.8})$$

$$727 \quad \frac{dR_{\text{N2}}^i}{dt} = F_{\text{mix},\text{N2}}^i - F_{\text{out},\text{N2}}^i + F_{\text{den}}^i \quad (\text{A.9})$$

728 for  $i = \{\text{low, high}\}$ .

729 **Shelf ocean**

$$730 \quad \frac{dR_{36\text{Ar}}^{\text{shelf}}}{dt} = F_{\text{mix},36\text{Ar}}^{\text{shelf}} - F_{\text{as},36\text{Ar}}^{\text{atm-shelf}} \quad (\text{A.10})$$

$$731 \quad \frac{dR_{40\text{Ar}}^{\text{shelf}}}{dt} = F_{\text{rd}}^{\text{shelf}} + F_{\text{mix},40\text{Ar}}^{\text{shelf}} - F_{\text{as},40\text{Ar}}^{\text{atm-shelf}} \quad (\text{A.11})$$

$$732 \quad \frac{dR_{40\text{K}}^{\text{shelf}}}{dt} = F_{\text{mix},40\text{K}}^{\text{shelf}} - F_{\text{rd}}^i + F_{\text{w},40\text{K}} \quad (\text{A.12})$$

$$733 \quad \frac{dR_{\text{K}}^{\text{shelf}}}{dt} = F_{\text{mix},\text{K}}^i + F_{\text{w},\text{K}} \quad (\text{A.13})$$

$$734 \quad \frac{dR_{\text{PO4}}^{\text{shelf}}}{dt} = F_{\text{mix},\text{PO4}}^{\text{shelf}} - F_{\text{EXT}}^{\text{shelf}} + F_{\text{remin},\text{PO4}}^{\text{shelf}} + F_{\text{w},\text{PO4}} - F_{\text{NO3}}^{\text{shelf}} \quad (\text{A.14})$$

$$735 \quad \frac{dR_{\text{NO3}}^{\text{shelf}}}{dt} = F_{\text{mix},\text{NO3}}^{\text{shelf}} - F_{\text{out},\text{NO3}}^{\text{shelf}} + F_{\text{nit}}^{\text{shelf}} - F_{\text{den}}^{\text{shelf}} + F_{\text{remin},\text{NO3}}^{\text{shelf}} - F_{\text{NO3}}^{\text{shelf}} \quad (\text{A.15})$$

$$736 \quad \frac{dR_{\text{NH4}}^{\text{shelf}}}{dt} = F_{\text{mix},\text{NH4}}^{\text{shelf}} - F_{\text{out},\text{NH4}}^{\text{shelf}} - F_{\text{nit}}^{\text{shelf}} + F_{\text{remin},\text{NH4}}^{\text{shelf}} + F_{\text{w},\text{NH4}} - F_{\text{seddiff}}^{\text{shelf}} \quad (\text{A.16})$$

$$737 \quad \frac{dR_{\text{N2}}^{\text{shelf}}}{dt} = F_{\text{mix},\text{N2}}^{\text{shelf}} - F_{\text{out},\text{N2}}^{\text{shelf}} + F_{\text{den}}^{\text{shelf}} \quad (\text{A.17})$$

738

**Deep ocean**

$$\frac{dR_{40Ar}^{deep}}{dt} = F_{mix,40Ar}^{deep} + F_{rd}^{deep} - F_{hydro,40Ar}^{deep} + F_{ogmor,40Ar} \quad (A.18)$$

$$\frac{dR_{36Ar}^{deep}}{dt} = F_{mix,36Ar}^{deep} - F_{hydro,36Ar}^{deep} + F_{ogmor,36Ar} \quad (A.19)$$

$$\frac{dR_{40K}^{deep}}{dt} = F_{mix,40K}^{deep} - F_{rd}^{deep} - F_{hydro,40K} + F_{ogmor,40K} \quad (A.20)$$

$$\frac{dR_K^{deep}}{dt} = F_{mix,K}^{deep} - F_{hydro,K} + F_{ogmor,K} \quad (A.21)$$

$$\frac{dR_{PO4}^{deep}}{dt} = F_{mix,PO4}^{deep} + F_{remin,PO4}^{deep} - F_{hydro,PO4} + F_{ogmor,PO4} \quad (A.22)$$

$$\frac{dR_{NO3}^{deep}}{dt} = F_{mix,NO3}^{deep} + F_{remin,NO3}^{deep} + F_{nit}^{deep} - F_{den}^{deep} - F_{hydro,NO3}^{deep} \quad (A.23)$$

$$\frac{dR_{NH4}^{deep}}{dt} = F_{mix,NH4}^{deep} - F_{nit}^{deep} + F_{remin,NH4}^{deep} - F_{seddif}^{deep} - F_{hydro,NH4}^{deep} \quad (A.24)$$

$$\frac{dR_{N2}^{deep}}{dt} = F_{mix,N2}^{deep} + F_{den}^{deep} + F_{ogmor,N} \quad (A.25)$$

747

**Sediments**

$$\frac{dR_{NO3}^i}{dt} = F_{nit}^i - F_{den}^i + F_{seddif,NO3}^{iii} \quad (A.26)$$

$$\frac{dR_{NH4}^i}{dt} = F_{remin,NH4}^i - F_{nit}^i + F_{seddif,NH4}^{iii} \quad (A.27)$$

$$\frac{dR_{PO4}^i}{dt} = F_{remin,PO4}^i + F_{seddif}^{iii} \quad (A.28)$$

$$\frac{dR_N^i}{dt} = F_{bur,NH4}^i - F_{sub,NH4}^{ii} \quad (A.29)$$

$$\frac{dR_{PO4}^{ii}}{dt} = F_{bur,PO4}^i - F_{sub,PO4}^{ii} \quad (A.30)$$

753 for  $i = \{\text{reactive shelf sediments, reactive deep sediments}\}$ ,  $ii = \{\text{shelf sediments, deep}$   
 754  $\text{sediments}\}$ , and  $iii = \{\text{shelf ocean, deep ocean}\}$ .

755

**Ocean crust**

$$\frac{dR_{40Ar}^i}{dt} = F_{rd} - F_{sub,40Ar}^i \quad (A.31)$$

$$\frac{dR_{40K}^i}{dt} = -F_{rd} - F_{sub,40K}^i \quad (A.32)$$

$$\frac{dR_K^i}{dt} = F_{hydro,K} - F_{sub,K}^i \quad (A.33)$$

$$\frac{dR_N^i}{dt} = F_{hydro,N} - F_{sub,NH4}^i \quad (A.34)$$

$$\frac{dR_{PO4}^i}{dt} = F_{hydro,PO4} - F_{sub,PO4}^i \quad (A.35)$$

761 for  $i = \{\text{ocean crust}\}$ .

**Continental crust**

$$\frac{dR_{40\text{Ar}}^i}{dt} = F_{\text{rd}}^i - F_{\text{w},40\text{Ar}} \quad (\text{A.36})$$

$$\frac{dR_{40\text{K}}^i}{dt} = -F_{\text{rd}}^i - F_{\text{w},40\text{K}} \quad (\text{A.37})$$

$$\frac{dR_j^i}{dt} = F_{\text{cg},j} - F_{\text{w},j} \quad (\text{A.38})$$

for  $i = \{\text{continental crust}\}$  and  $j = \{\text{K}, \text{NH}_4^+, \text{PO}_4^{3-}\}$ .

**Mantle**

$$\frac{dR_{40\text{Ar}}^i}{dt} = F_{\text{rd}}^i - F_{\text{ogm},40\text{Ar}} + F_{\text{subnet},40\text{Ar}} \quad (\text{A.39})$$

$$\frac{dR_{40\text{K}}^i}{dt} = -F_{\text{rd}}^i - F_{\text{ogm},40\text{K}} + F_{\text{subnet},40\text{K}} \quad (\text{A.40})$$

$$\frac{dR_j^i}{dt} = -F_{\text{ogmor},j} + F_{\text{subnet},j} \quad (\text{A.41})$$

for  $i = \{\text{mantle}\}$  and  $j = \{^{36}\text{Ar}, \text{N}, \text{PO}_4^{3-}, \text{and K}\}$ .

**B: Calculating initial N distribution**

We use the following equation from *Libourel et al.* [2003] to calculate the starting amount of N in the atmosphere and mantle for the nominal run:

$$N_{2, \text{magma}} = 2.21 \times 10^{-9} \text{pN}_2 + fO_2^{-0.75} 2.13 \times 10^{-17} \text{pN}_2^{0.5} \quad (\text{B.1})$$

where  $\text{pN}_2$  is in atmospheres and  $N_{2, \text{magma}}$  is in  $\text{mol g}^{-1} \text{atm}^{-1}$ . We chose an  $fO_2$  of IW-2 ( $fO_2 = 10^{-11.4}$ ), where IW is the iron wüstite buffer, which is the expected oxygen fugacity of the magma ocean immediately after core formation [*Wood et al.*, 2006] (Fig. B.1).

Then, for a variety of  $\text{pN}_2$  values, we calculate a magma  $\text{N}_2$  concentration at  $fO_2 = \text{IW-2}$ , and multiply this concentration by the mass of the mantle. This assumes the whole mantle equilibrated during the atmosphere during the magma ocean phase.

Finally, we describe the fraction of the total N budget that is in the atmosphere based on the above solubility calculations. This figure ultimately guided our choice for total N budget and starting atmospheric N mass in the nominal run. We chose 4.5 PAN as the total budget, which results in 82% of the total N starting in the atmosphere. The total N budget was chosen so that the nominal run resulted in a 1 PAN modern atmosphere at the end of the model run.

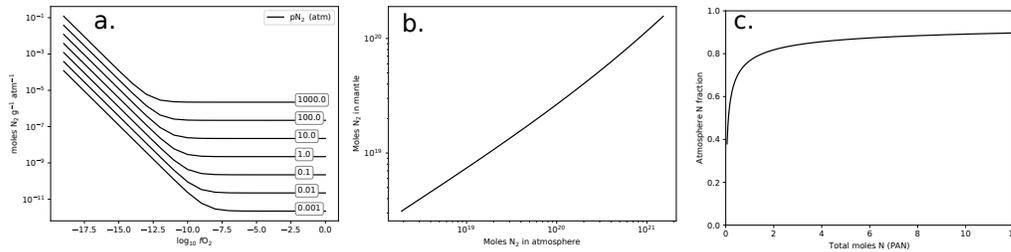


Figure B.1: Nitrogen solubility in basaltic magma used to calculate starting atmospheric N. a.) Basaltic magma  $N_2$  content as a function of oxygen fugacity. Lines are for different  $pN_2$ , with pressure in atmospheres shown in boxes. Modified after *Libourel et al.* [2003]. b.) Total mantle and atmospheric N based on the solubility experiments of *Libourel et al.* [2003] at the end of core formation. c.) Atmospheric fraction of N as a function of total N (PAN) for an atmosphere in equilibrium with the mantle at the end of the magma ocean phase. Oxygen fugacity is IW - 2.

### 788 C: Argon and potassium model performance checks

789 We use argon concentration in the atmosphere as a check on the performance of  
 790 degassing and air-sea gas exchange in the model. The model overestimates the modern  
 791 day ratio of  $^{40}\text{Ar}/^{36}\text{Ar}$  in the atmosphere by about 1.5 fold (Fig. C.1). It is possible that  
 792 this slight overestimate is due in part to the model underestimating K concentration in the  
 793 continental crust (Fig. C.1). Higher K-content in the crust would lead to more  $^{40}\text{Ar}$  in the  
 794 crust, through storage after radioactive decay of  $^{40}\text{K}$ , and would then lower the atmospheric  
 795 Ar-ratio.

796 While the model output reproduces the K content of the mantle well, it underesti-  
 797 mates the continental crust concentration. Weathering is simply proportional to concen-  
 798 tration in the model, and does not take into account either differences in weathering due  
 799 to biologic activity or continental growth over time. Given different amounts of crustal  
 800 growth over time [e.g., *Dhuime et al.*, 2012], the continents would evolve in their capacity  
 801 to store K over time. In addition, we do not consider the effects of continental lithospheric  
 802 roots or cratonic mass, which could serve to store K for long periods during Earth history.  
 803 Future iterations of the EarthN model should incorporate crustal growth scenarios.

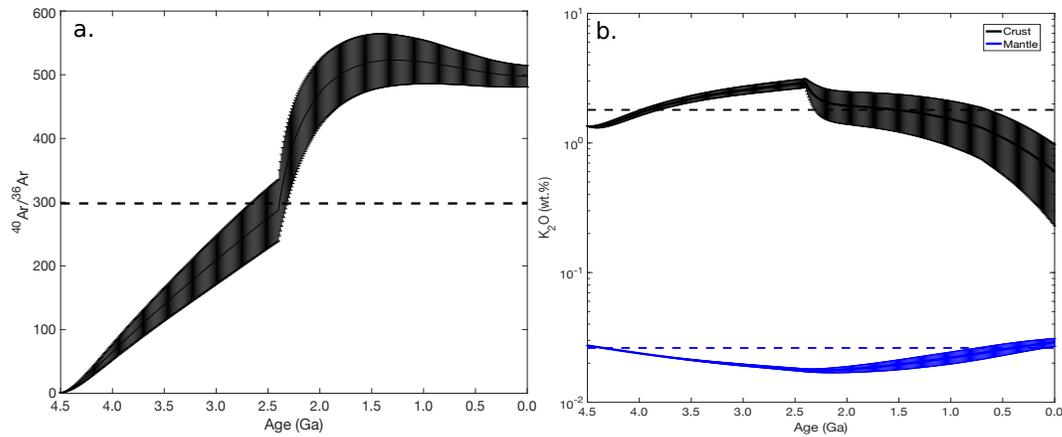


Figure C.1: Atmospheric  $^{40}\text{Ar}/^{36}\text{Ar}$  and K concentrations (wt. % $\text{K}_2\text{O}$ ) for continental crust and mantle from Monte Carlo runs. The mean and one standard deviation are shown, and modern values are given as dashed line [Rudnick and Gao, 2014; Arevalo et al., 2013].

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