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Modeling pN_2 through Geological Time: Implications for Planetary Climates and Atmospheric Biosignatures

E.E. Stüeken,[1,2,3,4] M.A. Kipp,[1,4] M.C. Koehler,[1,4] E.W. Schwieterman,[2,4,5]
B. Johnson,[6] and R. Buick[1,4]

Abstract

Nitrogen is a major nutrient for all life on Earth and could plausibly play a similar role in extraterrestrial biospheres. The major reservoir of nitrogen at Earth's surface is atmospheric N_2, but recent studies have proposed that the size of this reservoir may have fluctuated significantly over the course of Earth's history with particularly low levels in the Neoarchean—presumably as a result of biological activity. We used a biogeochemical box model to test which conditions are necessary to cause large swings in atmospheric N_2 pressure. Parameters for our model are constrained by observations of modern Earth and reconstructions of biomass burial and oxidative weathering in deep time. A 1-D climate model was used to model potential effects on atmospheric climate. In a second set of tests, we perturbed our box model to investigate which parameters have the greatest impact on the evolution of atmospheric pN_2 and consider possible implications for nitrogen cycling on other planets. Our results suggest that (a) a high rate of biomass burial would have been needed in the Archean to draw down atmospheric pN_2 to less than half modern levels, (b) the resulting effect on temperature could probably have been compensated by increasing solar luminosity and a mild increase in pCO_2, and (c) atmospheric oxygenation could have initiated a stepwise pN_2 rebound through oxidative weathering. In general, life appears to be necessary for significant atmospheric pN_2 swings on Earth-like planets. Our results further support the idea that an exoplanetary atmosphere rich in both N_2 and O_2 is a signature of an oxygen-producing biosphere. Key Words: Biosignatures—Early Earth—Planetary atmospheres. Astrobiology 16, 949–963.

1. Introduction

Life as we know it is implausible without nitrogen. It is an essential major nutrient for all living things because it is a key component of the nitrogenous bases in the nucleic acids that store, transcribe, and translate genetic information, a necessary ingredient of the amino acids constituting the proteins responsible for most cellular catalysis and at the core of the ATP molecule that is the principal energy transfer agent for biological metabolism. As nitrogen's cosmic abundance is only slightly less than that of carbon and oxygen and because it condenses at moderate distances in circumstellar disks, it should have been available to other potential exoplanetary biospheres. However, N_2 gas, the most likely nitrogen species near planetary surfaces in the habitable zone, is nearly inert at standard conditions because of the very strong triple bond in N≡N. Lightning can break this bond and combine nitrogen with other atmospheric species, but on Earth this process has been relatively inefficient (Borucki and Chameides, 1984; Navarro-González *et al.*, 2001). Much more significant for removing N_2 from Earth's atmosphere is microbial N_2 fixation to ammonium, a reaction catalyzed by the enzyme nitrogenase. Today, most of this fixed nitrogen is returned to the atmosphere via the biogeochemical nitrogen cycle, a series of microbially modulated redox reactions that ultimately transform organic nitrogen back to gaseous N_2. Thus, life's demand for nitrogen regulates its atmospheric abundance.

[1]Department of Earth and Space Sciences and Astrobiology Program, University of Washington, Seattle, Washington, USA.
[2]Department of Earth Sciences, University of California, Riverside, California, USA.
[3]Department of Earth and Environmental Sciences, University of St Andrews, St Andrews, Scotland, UK.
[4]NASA Astrobiology Institute's Virtual Planetary Laboratory, Seattle, Washington, USA.
[5]Department of Astronomy and Astrobiology Program, University of Washington, Seattle, Washington, USA.
[6]School of Earth and Ocean Sciences, University of Victoria, Victoria, Canada.

Though N_2 is not a greenhouse gas itself, its atmospheric partial pressure affects planetary environmental conditions. Higher N_2 pressure can enhance greenhouse warming by pressure broadening the absorption bands of such gases as water vapor, CO_2, CH_4, and N_2O (Goldblatt *et al.*, 2009). Hence, the partial pressure of N_2 indirectly influences surface temperature and thus habitability. Moreover, a low total atmospheric pressure of all gases combined weakens the cold-trap for water vapor at the tropopause (Wordsworth and Pierrehumbert, 2014). Where N_2 is a major atmospheric constituent, a drop in pN_2 can make the tropopause cold-trap leaky (Zahnle and Buick, 2016), allowing water vapor into the upper layers of the atmosphere where it can either remain as vapor, perhaps increasing overall greenhouse warming (Rind, 1998; Solomon *et al.*, 2010; Dessler *et al.*, 2013) (but for a contrary view see Huang *et al.*, 2016), or freeze as high-altitude ice clouds in polar regions, warming the high latitudes and making planetary climate more equable (Sloan and Pollard, 1998). Thus, planetary habitability is dependent, at least in part, on atmospheric nitrogen levels.

Though we know next to nothing about the evolution of the biogeochemical nitrogen cycles on other planets, we now have a better-resolved picture of the behavior of nitrogen through Earth's history (Ader *et al.*, 2016; Stüeken *et al.*, 2016). It seems that (1) microbial nitrogen fixation evolved very early in Earth's history such that a nitrogen crisis for the primordial biosphere was averted (Stüeken *et al.*, 2015; Weiss *et al.*, 2016), (2) the partial pressure of atmospheric N_2 has fluctuated through time to a greater degree than previously anticipated (Som *et al.*, 2016), (3) an aerobic nitrogen cycle arose before the Great Oxidation Event (GOE) at ~2.35 Ga (Garvin *et al.*, 2009; Godfrey and Falkowski, 2009), (4) during the mid-Proterozoic aerobic and anaerobic nitrogen cycling was spatially separated under low-oxygen conditions (Stüeken, 2013; Koehler *et al.*, 2016), and (5) a modern nitrogen cycle with widespread aerobic activity did not arise until the late Neoproterozoic (Ader *et al.*, 2014). The main constraints on these developments were evidently biological evolution and redox changes in Earth's surface environments, principally the oxygenation state of the atmosphere and ocean (Stüeken *et al.*, 2016). Other Earth-like planets may have evolved along somewhat similar pathways with respect to nitrogen cycling, provided that they also originated Earth-like life. If so, then atmospheric swings in pN_2 may be a common feature of terrestrial inhabited planets.

In the present study, we investigated the diversity of terrestrial planetary nitrogen cycles by modeling the evolution of Earth's atmospheric N_2 reservoir. We then perturbed the model to examine several ahistorical extreme scenarios that could arise on Earth-like exoplanets, defined here as planets with a silicate rock mantle and iron core (empirically <1.6 Earth radii in size, Rogers, 2015), an orbit within the conservative limits of the habitable zone (Kopparapu *et al.*, 2013), and a similar volatile content to Earth. This conservative definition prescribes a high-molecular-weight atmosphere dominated by N_2, CO_2, and H_2O rather than H_2 (*cf.* Pierrehumbert and Gaidos, 2011; Seager, 2013). After exploring a range of variables, we concluded that some combinations of N_2 abundance with other gases could act as extraterrestrial biosignatures, others could be "false positives," and yet others may indicate that a planet is uninhabited. Overall, our results suggest that an anaerobic biosphere can greatly facilitate the removal of large amounts of N_2 from a planetary atmosphere.

2. Model Setup

2.1. Biogeochemical nitrogen box model

We used the isee Stella software to construct a box model of the global biogeochemical nitrogen cycle (Fig. 1), tracking total nitrogen. Boxes included the atmosphere, pelagic marine sediments deposited on oceanic crust, continental marine sediments deposited on continental shelves and in epeiric seas, continental crust, and the mantle. Continental marine sediments were defined to become part of the continental crust after 100 million years and from there onward were subjected to metamorphism, which returns nitrogen to the atmosphere. Similarly, we let pelagic marine sediments accumulate for 100 million years before they were subjected to subduction, metamorphism, and volcanism. These timescales were based on the observation that C/N ratios in sedimentary rocks older than about 100 million years become more variable with higher average values (Algeo *et al.*, 2014). The two sinks of nitrogen from the atmosphere were burial in pelagic sediments and burial in continental sediments with proportions of ~1:25 (Berner, 1982). The sources of atmospheric nitrogen were volcanic and metamorphic degassing of subducted pelagic sediments, metamorphism of continental crust, oxidative weathering of continents, and mantle outgassing. Denitrification was not explicitly included as a source, because we did not track the marine nitrogen reservoir.

The model was run in 1-million-year time-steps from 4.5 Ga to the present. Differential equations listed in the Supplementary Material were solved with the Euler method (Supplementary Material is available online at www.liebertonline.com/ast). The chosen step size is much lower than the residence time of nitrogen in our modeled reservoirs (>100 million years), which eradicates computational artifacts that can result in mass imbalances. The initial abundances of nitrogen in the mantle, continental crust, and sediments were set such that the concentrations were the same, assuming that any disequilibrium in concentrations observed today is due to biogeochemical overprinting. The rock masses and modern nitrogen inventories were taken from the work of Johnson and Goldblatt (2015). The initial abundance of atmospheric N_2 is unknown. We tuned the model such that the final atmospheric N_2 abundance after 4.5 billion years equaled the modern amount of $2.87 \cdot 10^{20}$ mol, defined as one times present atmospheric nitrogen (PAN) (Johnson and Goldblatt, 2015).

A more detailed description of how rate constants were derived is given in the Supplementary Material. Following the work of Berner (2006), nitrogen burial was parameterized through biomass burial (*i.e.,* organic carbon). Although this approach neglects the origin and radiation of biological nitrogen metabolisms over Earth's history (Stüeken *et al.*, 2016), it is preferred because (a) it avoids major uncertainties about metabolic rates in deep time and (b) it is sufficient for tracking the total nitrogen sink from the atmosphere. As further discussed below (Section 4.1), additional nitrogen burial through adsorption on clay minerals is negligible compared to the organic nitrogen flux into

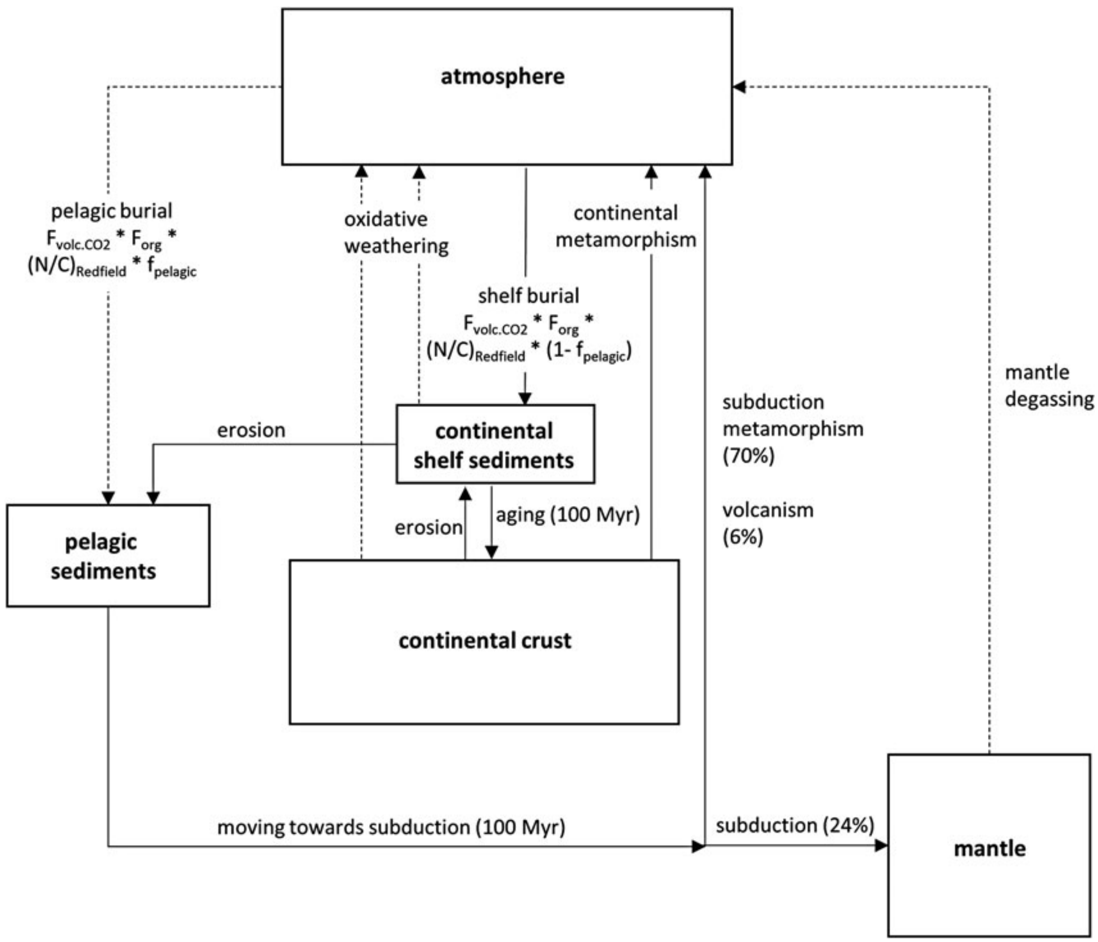

FIG. 1. Schematic of the nitrogen model for Earth. All fluxes except for burial of nitrogen from the atmosphere into sediments are dependent on the reservoir size. Fluxes with dashed arrows are implemented as time-variable, except in our ''base model'' (Fig. 2a).

sediments. Using this approach, we calculated modern nitrogen burial from the modern volcanic CO_2 outgassing flux of $6 \cdot 10^{18}$ mol/Myr (Marty and Tolstikhin, 1998), assuming that 22% ($f_{org} = 0.22$) of volcanogenic CO_2 is buried as organic carbon in the absence of land plants (pre-Devonian) (Krissansen-Totton *et al.*, 2015) and that the C/N ratio of post-diagenetic marine biomass is approximately 10 (Godfrey and Glass, 2011; Algeo *et al.*, 2014). This gave a nitrogen burial flux of $1.32 \cdot 10^{17}$ mol/Myr, equal to $\sim 1.5\%$ of modern biological N_2 fixation ($8.64 \cdot 10^{18}$ mol/Myr) (Galloway *et al.*, 2004). We then modulated this flux in deep time in three different ways. First, we took into account secular trends in f_{org} as inferred from the carbon isotope record (''F_{org} model'') (Krissansen-Totton *et al.*, 2015). Uncertainties in this record, resulting from potentially underrepresented carbonate reservoirs (Bjerrum and Canfield, 2004; Schrag *et al.*, 2013) and the variance in $\delta^{13}C$ values at any given time point, are discussed below. Second, we assumed a gradual decline in CO_2 outgassing from the Hadean to the modern, following the parameterization of Canfield (2004, Eq. 2) (''F_{org} + Heatflow model''). By mass balance, higher CO_2 outgassing in the earlier Precambrian implies higher burial fluxes of biomass and with it nitrogen. Uncertainties and caveats of this approach are discussed below. Third, we tested for the effects of additional 2-fold increases in CO_2 input, and hence, nitrogen burial, during superplume events (Abbott and Isley, 2002) (''F_{org} + Heatflow + Superplume model''). This model did not include potential N_2 addition through enhanced volcanism, which we will discuss separately. In all these models, oxidative weathering was implemented as a function of pO_2 through time (Lyons *et al.*, 2014) with a reaction order of 0.5, that is, proportional to $(pO_2)^{0.5}$ (Chang and Berner, 1999; Bolton *et al.*, 2006).

In a separate set of models, we tested hypothetical scenarios for Earth-like planets without any biosphere and an anoxic atmosphere, or with a completely anaerobic biosphere that does not experience oxygenation events. Our definition of Earth-like planets includes an orbit within the habitable zone where liquid water can be stable at the surface, as well as a rocky composition and a volatile inventory similar to those of Earth (Section 1). This definition is admittedly limited, but it allows us to identify with greater confidence a subset of parameters that can play a critical role in the history of the nitrogen cycle. We assumed abiotic nitrogen burial was driven by NH_4^+ adsorption on clay minerals after abiotic N_2 reduction in the atmosphere. Rates were taken from the work of Stüeken (2016) for two extreme end-members corresponding to high and low estimates of abiotic N_2 fixation rates for Archean Earth and seawater pH of 5 and 8, respectively (see Supplementary Material S1.1). For illustration, these burial fluxes are equal to $1.4 \cdot 10^{-1}$ and $1.7 \cdot 10^{-5}$ times the modern nitrogen burial described above. We did not test abiotic burial under oxic conditions because in that case NH_4^+ production would likely be low and nitrogen burial trivial. For the ''biotic anoxic'' scenario, we used nitrogen burial rates equal to 1–10% of the modern biological N_2 fixation rate. In both the abiotic and biotic anoxic model, oxidative weathering was switched off.

Rate constants for oxidative weathering, metamorphism, erosion, subduction, volcanism, and outgassing were calculated as the ratio of modern fluxes to modern reservoir sizes (see Supplementary Material for details). We further performed simple order-of-magnitude estimates of catastrophic events, such as impacts and large volcanic eruptions, to test whether these could affect our overall conclusions (Section 3.3).

2.2. Modeling effects on greenhouse gases and global climate

We selected the most extreme end-members of our Earth model to determine potential effects on Earth's climate. As shown below, the timescales over which variations in pN_2 can occur exceed those of the carbonate-silicate feedback cycle (Walker *et al.*, 1981). Hence, changing pN_2 alone is unlikely to cause rapid climate changes, because pCO_2 can rapidly re-adjust to keep surface temperatures more or less steady. We therefore decided to calculate the required changes in pCO_2 that would counterbalance the effects of varying pN_2. We used an iterative approach to determine the pCO_2 necessary to maintain a 278 K globally averaged surface temperature (T_{GAT}), equivalent to the estimated globally averaged temperature during the last glacial maximum. This limit was chosen because geological evidence suggests that the Archean was cool (Hren *et al.*, 2009; Blake *et al.*, 2010) but not permanently glaciated (Young, 1991; de Wit and Furnes, 2016). As input values, we used the changes in nitrogen abundance shown in Section 3 (Fig. 2) and changes in solar luminosity from 3.5 to 2.4 Ga. To do this, we used a 1-D radiative convective model that was recently used to calculate habitable zone boundaries (Kasting *et al.*, 1984, 1993; Kopparapu *et al.*, 2013) and characterize the surface temperature of a hypothetical Archean Earth with a global hydrocarbon haze (Arney *et al.*, 2016). We chose a surface albedo of $A_{surf} = 0.32$, which is a tuning parameter used to reproduce the temperature of modern Earth (Kopparapu *et al.*, 2013; Arney *et al.*, 2016). Our atmospheric composition consisted of only N_2, CO_2, H_2O, and CH_4, where the pN_2 was taken from our model output (Table 1) and CH_4 was fixed at $pCH_4 = 0.001$ (fCH_4, fCO_2, fN_2, and the total surface pressure P_0 were adjusted self-consistently for changes in pCO_2). The H_2O profiles were calculated using a relative humidity profile assuming a surface relative humidity of 80% (Manabe and Wetherald, 1967). The solar luminosity at 3.5 and 2.4 Ga (0.769 and 0.831) was found through interpolation of Table 2 in the work of Bahcall *et al.* (2001). We focused on the pCO_2 required to maintain a $T_{GAT} > 278$ K, noting that significantly lower temperatures ($T_{GAT} < 273$ K) may allow some open oceans, but a 3-D model would be needed to capture their additional complexities (see Supplementary Material S5 for limitations of our approach). Table 1 shows a summary of our results. We also indicate the surface temperature if pCO_2 was not adjusted to maintain $T_{GAT} = 278$ K, but was maintained at the pCO_2 value at 3.5 Ga, and if both the pCO_2 and solar luminosity were maintained at the 3.5 Ga values. Table 2 shows similar results as Table 1 but for a more permissive initial and final T_{GAT} of 273 K. This illustrates the sensitivity of the required pCO_2 adjustment to compensate for pN_2 drawdown as a function of the choice of reference temperature.

3. Results

3.1. Nitrogen burial constrained by carbon burial

We tested four different models for the evolution of nitrogen burial through geological time (Fig. 2). In our base model (Fig. 2a), nitrogen burial was held constant at its modern flux. Each subsequent iteration incorporates an additional parameter to the N burial record and, thus, shows additional atmospheric N drawdown. Sensitivity tests are presented in Section S3. The majority of the uncertainty range illustrated in Fig. 2 derives from uncertainties about rates of nitrogen loss during continental metamorphism.

3.1.1. F_{org} model. In the first test, the base model was modified by scaling nitrogen burial as a function of f_{org} (organic carbon burial fraction). This did not significantly change the evolutionary trend of the atmospheric nitrogen reservoir predicted by the base model, as f_{org} has been relatively invariant through geological time (Fig. 2b). During the largest burial event indicated by the carbon isotope record, the Lomagundi Event at *ca.* 2.3–2.1 Ga, f_{org} temporarily exceeds 0.3 (Precambrian baseline $\sim$0.15–0.2). However, even this increase in organic burial alone appears to be insufficient to significantly deplete the atmospheric N_2 reservoir by more than $\sim$0.02 PAN. This model shows a slow depletion of the atmospheric nitrogen reservoir during the Archean (from 1.0 to 0.81 PAN) and relatively constant atmospheric nitrogen during the Proterozoic (range 0.78 to 0.82 PAN). Modern atmospheric nitrogen levels are not attained until late in the Phanerozoic.

3.1.2. F_{org} + Heatflow model. When we scale nitrogen burial proportionally to the amount of CO_2 outgassing (Canfield, 2004), our model shows a significant drawdown of atmospheric nitrogen during the Archean, reaching a minimum of 0.44 PAN (= 0.35 bar N_2) in the earliest Paleoproterozoic, immediately prior to the GOE (Fig. 2c). Fixed nitrogen is principally buried and stored in continental sediments and continental crust, which reach a maximum of 1.7× the modern continental reservoir size at this time (Section S2). During the GOE, the atmospheric nitrogen reservoir rebounds due to enhanced oxidative weathering of the continents, but this rebound stops after the GOE, and atmospheric nitrogen remains low at 0.59–0.65 PAN (= 0.47–0.51 bar N_2) until the Neoproterozoic Oxidation Event (NOE). Atmospheric N_2 rapidly rises during the Neoproterozoic and Paleozoic in response to a further enhancement of oxidative weathering with the second rise of O_2. The later Phanerozoic shows a slow gradual increase in

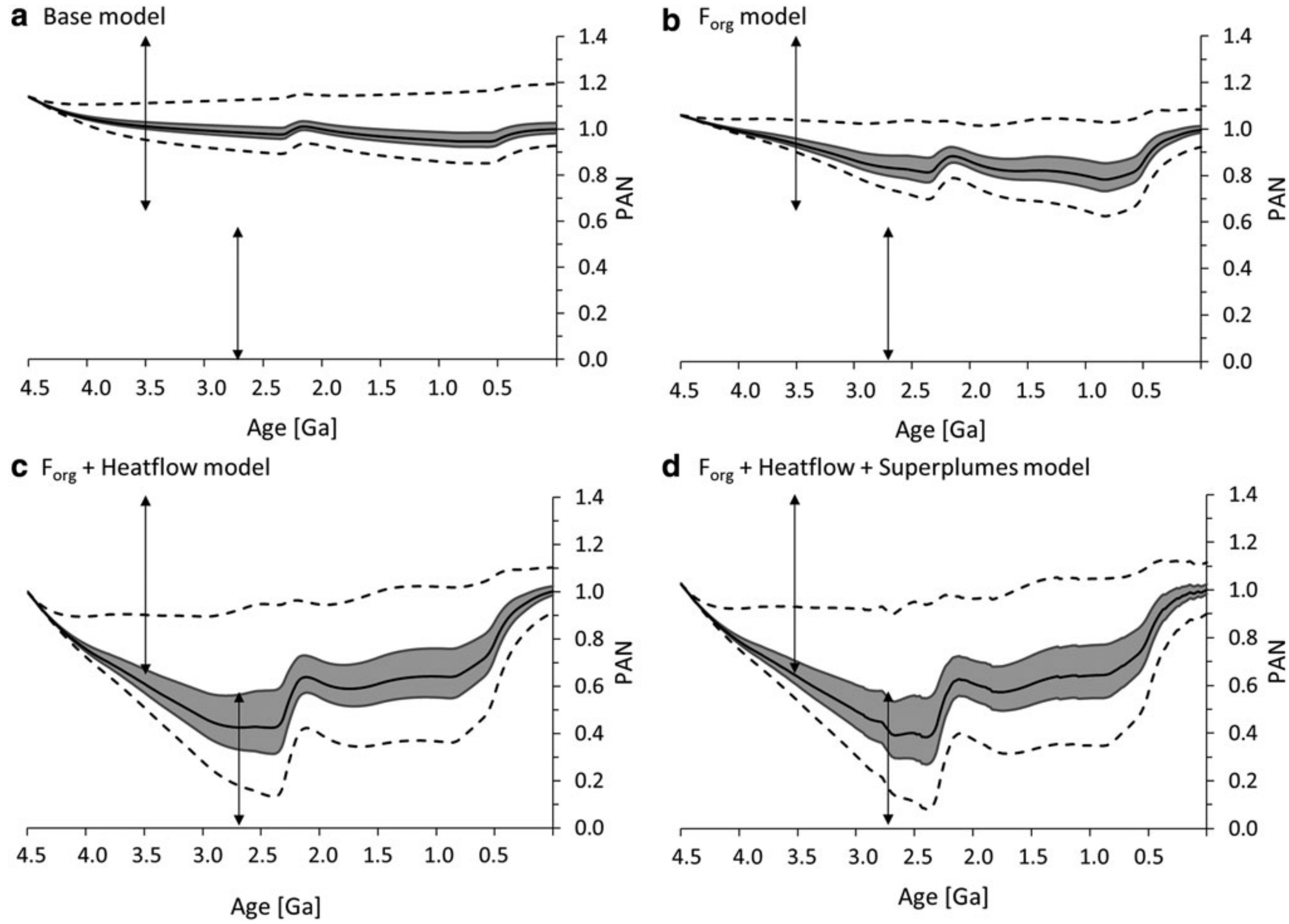

FIG. 2. Reconstructing nitrogen burial over Earth's history. Arrows mark pN_2 value inferred for proxies (Marty *et al.*, 2013; Som *et al.*, 2016). (**a**) Base model. N burial is held constant, calculated as the product of volcanic CO_2 outgassing, the pre-Devonian organic burial fraction (f_{org}) of 0.22, and the inverse of the Redfield C/N ratio of 10. (**b**) F_{org} model. N burial is modulated by secular changes in f_{org} as inferred from the carbon isotope record (Krissansen-Totton *et al.*, 2015). (**c**) F_{org} + Heatflow model. CO_2 outgassing is assumed to have declined gradually from the Hadean to the modern with decreasing heatflow from Earth's interior, as described by Canfield (2004). Carbon burial and with it nitrogen burial is changed in proportion. Mantle outgassing is modulated in the same way. (**d**) F_{org} + Heatflow + Superplumes model. Additional pulses of CO_2 outgassing are assumed during intervals of superplumes as recorded in the rock record (Abbott and Isley, 2002). Solid black line = using best estimates for all parameters; dashed lines = most extreme uncertainty interval if all parameters are off in the same direction (excluding uncertainties in Redfield ratio and modern CO_2 outgassing, Supplementary Material S3); gray shaded area = more plausible uncertainty interval with narrower range of values for the metamorphic rate constant (most sensitive variable, see Supplementary Material S3).

Table 1. Climate Response to Changes in Atmospheric N_2

Line	*Age (Ga)*	*Rel. solar luminosity*	*N_2 (PAN)*	pN_2 *(bar)*	pCO_2 *(bar)*	pCH_4 *(bar)*	P_0 *(bar)*	T_{GAT} *(K)*
F_{org} + Heatflow model:								
1	3.5	0.769	0.61	0.476	0.046	0.001	0.523	278.0
2	2.4	0.769	0.42	0.328	0.046	0.001	0.375	274.7
3	2.4	0.831	0.42	0.328	0.046	0.001	0.375	282.4
4	2.4	0.831	0.42	0.328	0.018	0.001	0.346	278.0
F_{org} + Heatflow + Superplumes model, lower limit:								
1	3.5	0.769	0.54	0.421	0.056	0.001	0.480	278.0
2	2.4	0.769	0.08	0.062	0.056	0.001	0.119	264.8
3	2.4	0.831	0.08	0.062	0.056	0.001	0.119	270.6
4	2.4	0.831	0.08	0.062	0.160	0.001	0.223	278.0

Input data are the age, the corresponding relative solar luminosity taken from Bahcall *et al.* (2001), atmospheric N_2 (PAN) calculated from our box model, and an assumed constant background level of 1000 ppmv CH_4. Partial N_2 pressure (pN_2) was calculated as the product of total N_2 in units of PAN and the modern pN_2 of 0.78 bar. Output parameters are T_{GAT} (global average surface temperature), pCO_2, and P_0 (total average surface pressure, *i.e.,* sum of all gases). Line 1 = starting conditions at 3.5 Ga; line 2 = changing PAN with constant luminosity and constant pCO_2 (taken from line 1); line 3 = changing PAN and luminosity with constant pCO_2; line 4 = changing PAN, luminosity, and pCO_2. Parameters are calculated such that the T_{GAT} at (1) and (4) converges to 278 K.

Table 2. Climate Response to Changes in Atmospheric N_2

Line	*Age (Ga)*	*Rel. solar luminosity*	*N_2 (PAN)*	*pN_2 (bar)*	*pCO_2 (bar)*	*pCH_4 (bar)*	*P_0 (bar)*	*T_{GAT} (K)*
F_{org} + Heatflow model:								
1	3.5	0.769	0.61	0.476	**0.020**	0.001	**0.497**	**273.2**
2	2.4	0.769	0.42	0.328	**0.020**	0.001	**0.348**	**270.6**
3	2.4	0.831	0.42	0.328	**0.020**	0.001	**0.348**	**278.4**
4	2.4	0.831	0.42	0.328	**0.005**	0.001	**0.333**	**273.2**
F_{org} + Heatflow + Superplumes model, lower limit:								
1	3.5	0.769	0.54	0.421	**0.024**	0.001	**0.446**	**273.2**
2	2.4	0.769	0.08	0.062	**0.024**	0.001	**0.087**	**261.1**
3	2.4	0.831	0.08	0.062	**0.024**	0.001	**0.087**	**266.2**
4	2.4	0.831	0.08	0.062	**0.118**	0.001	**0.181**	**273.2**

Same as Table 1, but for a fiducial T_{GAT} of 273.2 K at lines (1) and (4). Differences from Table 1 are in **bold**.

atmospheric N_2. As discussed below, we consider this model the most plausible mechanism for explaining a Neoarchean pressure minimum of 0.23 ± 0.23 bar as determined from basaltic amygdales (Som *et al.*, 2016).

3.1.3. F_{org} + Heatflow + Superplumes model. Scaling up N burial by a factor of 2 during plume intervals (Abbott and Isley, 2002) resulted in a small but noticeable effect on the atmospheric nitrogen reservoir (Fig. 2d). The effect is most pronounced during the longest superplume event in the geological record, which is thought to have lasted from 2.775 to 2.696 Ga. Atmospheric nitrogen is drawn down to 0.42 PAN (= 0.33 bar N_2) by 2.69 Ga in the wake of this event, which is also consistent with basalt amygdale paleobarometry estimates for 2.7 Ga (Som *et al.*, 2016).

To test the plausibility of greater burial enhancement factors, we explored the range from 1× to 10× burial enhancement during plume intervals. A 10× burial enhancement factor for superplume intervals caused the atmospheric nitrogen reservoir to become entirely depleted in the Neoarchean (0.0 PAN at 2.71 Ga), which is implausible because it would have driven the biosphere to near extinction by removing a major nutrient, or could have induced a global glaciation, for which there is no geological evidence at this time. We thus deemed 10× too extreme of a burial enhancement factor. Values less than 10× and greater than 1× are plausible, but given available data, it is difficult to derive accurate constraints. It is also quite possible that different plume events affected organic burial by different factors. Furthermore, as noted in Section 3.3, nitrogen outgassing from the mantle may have been more pronounced during superplume events, offsetting the effect of enhanced carbon burial. This effect was not considered in our model. All these complications make assessing the impact of plumes on the atmospheric nitrogen reservoir rather difficult. Still, it is worth noting that, even with a 2× burial enhancement, effects on the atmospheric nitrogen reservoir from plume events are small due to their short duration.

3.2. Atmospheric nitrogen evolution on abiotic and anoxic worlds

3.2.1. Abiotic anoxic planets. In the hypothetical scenario of a completely abiotic Earth-like planet in the habitable zone of another star with plausible abiotic nitrogen burial rates (Stüeken, 2016), the atmospheric nitrogen reservoir increased slightly from 1.0 PAN to 1.14–1.22 PAN after 4.5 billion years, with no periods of atmospheric N_2 drawdown (Fig. 3a). Catastrophic events such as plumes would have little effect on such a planet because, as further discussed below (Section 3.3.2), most of the nitrogen liberated by such events on Earth is likely sourced from the crust that has been enriched in nitrogen due to biological burial. On an abiotic planet, the crust would be relatively depleted in nitrogen. The sensitivity of these trends to changes in surface and deep Earth nitrogen fluxes is given in the Supplementary Material (Section S4). Overall, we find no plausible mechanism that could cause large swings in pN_2, apart from the possibility of atmospheric erosion (*e.g.*, Mars, Section 4.3) or freeze-out of N_2 on planets far outside the habitable zone (*e.g.*, Pluto). Although this modeled scenario is hypothetical, it emphasizes the potential importance of life for the evolution of the global nitrogen cycle.

3.2.2. Biotic anoxic planets. Our results for a hypothetical Earth-like planet with an anaerobic biosphere suggest that, under the right conditions, biological nitrogen drawdown can have a major effect on the evolution of atmospheric pN_2 through time. Nitrogen burial rates equal to 0.1 and 0.04 times the modern N_2 fixation rate sequester atmospheric nitrogen to 0 PAN by 4.1 and 2.9 Ga, respectively (Fig. 3b). The minimum flux required to reach 0 PAN within 4.5 billion years is roughly 0.03 times modern biological N_2 fixation, or 2 times the modern nitrogen burial flux. As in the case of our "F_{org} + Heatflow" model above, most of this nitrogen is stored in continental sediments and crust. A flux of 0.01 times modern biological N_2 fixation does not completely draw down atmospheric N_2 but leads to a steady state of ~0.84 PAN (Fig. 3b). A more detailed sensitivity analysis of these simulations is presented in Section S4. When other parameters are set to their most conservative values (*i.e.,* minimizing N_2 sequestration), a fixation flux of ~0.13 times modern would be needed to draw down atmospheric N_2 to 0 PAN. Again, this scenario is hypothetical, but in comparison to our Earth model, it emphasizes the important influence of atmospheric oxygen on the nitrogen cycle.

It is conceivable that a biosphere would go extinct when the atmospheric N_2 reservoir becomes depleted and triggers a global glaciation, at least if biological N_2 drawdown does

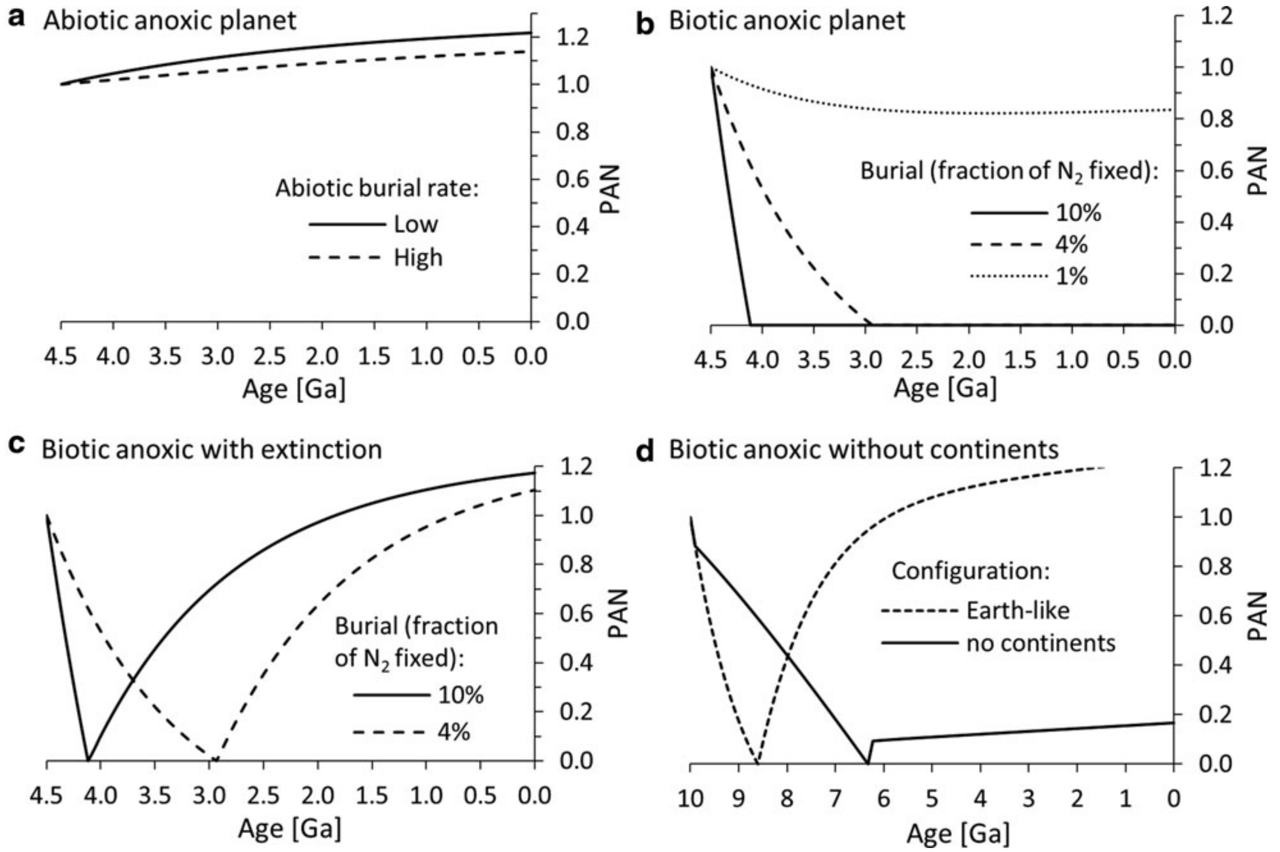

FIG. 3. Hypothetical evolution of atmospheric N_2 on extrasolar planets. (**a**) Abiotic anoxic planet where nitrogen burial is driven by NH_4^+ adsorption on clay minerals. High burial rate = $1.5 \cdot 10^{16}$ mol/Myr, low burial rate = $2.2 \cdot 10^{12}$ mol/Myr (Stüeken, 2016). (**b**) Biological anoxic planet without oxidative remineralization and weathering. Nitrogen burial is calculated as the product of the productivity factor and the modern biological N_2 fixation rate on Earth of $8.6 \cdot 10^{18}$ mol/Myr (Galloway *et al.*, 2004). (**c**) Biological anoxic planet with extinction of the biosphere upon atmospheric loss. (**d**) Anoxic biological burial and extinction as in (c) with and without burial on continental crust. The burial flux is set equal to 4% of modern biological N_2 fixation [dashed line in (d) describes the same scenario as dashed line in (c)]. Note change in scale on the *x* axis.

not slow down dramatically as pN_2 approaches 0 PAN (*e.g.*, Klingler *et al.*, 1989). Of course, in reality, biogeochemical feedbacks that were not considered in our model may maintain a low, but nonzero, N_2 reservoir in the atmosphere, and the biosphere may not necessarily go extinct as evidenced by extreme glacial events on Earth. We nevertheless explored this case in our model, because it provides an estimate of how fast pN_2 can recover on an anoxic planet in the absence of an Earth-like atmospheric oxygenation event (*cf.* Fig. 2c, 2d). Our results show that in this case the buried nitrogen would return much more slowly through continental metamorphism and erosion than it does with oxidative weathering. We determined the recovery time of atmospheric pN_2 after it is completely sequestered by switching off biological nitrogen fixation once atmospheric N_2 reached 0 PAN. With nitrogen burial fluxes of 10% and 4% modern N_2 fixation, it takes 2.76 and 2.62 billion years, respectively, for atmospheric nitrogen values to recover to 1.0 PAN, assuming that the biosphere does not recover during that time (Fig. 3c). This is much slower than the increases in pN_2 that occurred in our models over a few hundred million years after the GOE and NOE on Earth, which highlights the linkage between pO_2 and pN_2 that is further discussed below (Section 4.3).

To assess the effects of continental crust (the major nitrogen repository in our models), we ran a separate model where all burial was directed to pelagic sediments; that is, continents were bypassed to mimic a planet without an equivalent of continental crust. Burial fluxes were arbitrarily set to 4% times the modern fixation rate. Under these conditions, pN_2 drawdown to 0 PAN is much slower (Fig. 3d), because nitrogen in pelagic sediments has a much shorter residence time than in continental sediments and crust and is returned relatively rapidly through subduction-zone metamorphism and volcanism. However, once atmospheric N_2 has been sequestered in the mantle, it does not recover, even over a billion-year timescale. Although this model describes a purely hypothetical scenario of plate tectonics in the absence of continents, it demonstrates that a relatively shallow nitrogen repository akin to continental crust with an intermediate residence time between that of pelagic sediments and the mantle greatly facilitates large atmospheric pN_2 swings over hundreds of millions of years, as suggested for Precambrian Earth (Som *et al.*, 2016).

3.3. Catastrophic events

Planets are periodically subject to catastrophic events throughout their history. We performed order-of-magnitude calculations to test whether such events could affect atmospheric N_2 reservoirs and, hence, our overall conclusions. Possible events considered here include asteroid or comet impacts, superplume volcanism as an N_2 source, and large-scale planetary resurfacing.

3.3.1. Impacts. There are three ways impacts could affect the amount of nitrogen in a planetary atmosphere: direct nitrogen addition from the bolide, atmospheric erosion with loss of N_2 to space, and release of buried nitrogen through crustal heating. A variety of asteroids have substantial nitrogen contents. The most volatile rich are carbonaceous chondrites, which have 1235 ppm nitrogen on average (Wasson and Kallemeyn, 1988; Johnson and Goldblatt, 2015). If all nitrogen were released as N_2 upon impact, then a hypothetical $3.2 \cdot 10^{21}$ kg of carbonaceous chondrites could contribute 1 PAN. Such a mass is about 0.05% of Earth's mass and is approximately equivalent to the once-proposed total mass of late heavy bombardment material (Wetherill, 1975). Impacts later in the Archean, post-dating the Late Heavy Bombardment, would have been several orders of magnitude smaller than 0.05% of Earth's mass (Johnson and Melosh, 2012); hence this nitrogen source was most likely trivial for atmospheric evolution.

Impact erosion has been proposed as an explanation for the thin atmosphere of Mars (Melosh and Vickery, 1989), but more recent calculations suggest that this mechanism may have been less effective than previously thought (Manning *et al.*, 2009). The effect would further decrease with more massive planets than Mars; it is not generally considered to have been significant on early Earth. It is thus probably not a major nitrogen sink on most habitable Earth-like planets.

Large-scale crustal heating resulting from impacts could add some nitrogen to the atmosphere (Wordsworth, 2016). Current estimates of nitrogen in continental crust suggest a mass of $1.7 \cdot 10^{18}$ kg, or 0.5 PAN (Goldblatt *et al.*, 2009; Johnson and Goldblatt, 2015). During the late Archean, when atmospheric pN_2 may have been as low as 0.44 PAN (Section 3.1.2), the continental reservoir may have been as large as 1.7 times the present continental reservoir, though nitrogen concentrations in continental crust rocks through time are poorly constrained (Section S2). The nitrogen contained in oceanic crust and lithosphere is relatively minor ($\sim$0.57 to $0.67 \cdot 10^{18}$ kg N) (Johnson and Goldblatt, 2015). To raise atmospheric pN_2 by more than 0.1 PAN through crustal melting, more than 5% of the continental crust would have needed to melt in the Neoarchean and more than 20% in the modern. We consider this unlikely, because there is no geological evidence of such large-scale crustal melting events. We note, however, that some rock types, such as lower continental crust and the oceanic lithospheric upper mantle, are poorly characterized. There are suggestions that parts of the mantle may contain substantial nitrogen (Li *et al.*, 2015), and if a significant fraction of the mantle experienced melting, then large quantities of nitrogen could be added to the atmosphere.

3.3.2. Superplumes. Superplume events represent another type of mantle melting that may contribute to changes in atmospheric N_2. While typical mantle melts (*i.e.,* MORB) have a very low nitrogen content of $\sim$1 ppm (Marty, 1995; Marty and Zimmermann, 1999; Johnson and Goldblatt, 2015), sparse data from continental basalts show higher concentrations. Basalts from the Abitibi region have 6 ppm nitrogen (Honma, 1996), Columbia River basalt has 34 ppm (BCR-1, Govindaraju, 1994), and recent Antarctic basalts around 60 to 100 ppm (Greenfield, 1991). Assuming that most nitrogen will degas during eruption, these concentrations suggest that substantial nitrogen could have been released during flood basalt eruptive events.

Fluid in equilibrium with basaltic melt under oxidizing conditions ($f_{O2} = \Delta NNO + 3$) has approximately 10^4 times more nitrogen than the melt itself (Li *et al.*, 2015). Assuming all nitrogen contained in the fluid degasses, an eruption of $3 \cdot 10^{18}$ kg basalt (equivalent to the Siberian Traps) with $\sim$30 ppm nitrogen remaining in the basalt suggests a release of $1 \cdot 10^{18}$ kg nitrogen, or 0.25 PAN. While measurements of nitrogen in flood basalts are quite rare, making this speculative, this simple calculation hints that these events could influence atmospheric N_2 content. However, it is important to note that superplumes in oceanic plates would likely have been much less effective, given that marine basalts tend to have more than 1 order of magnitude less nitrogen than continental flood basalts (see above); the latter likely assimilate and liberate nitrogen from continental crust. An exception may be oceanic superplumes that pass through parts of the mantle that are enriched in nitrogen due to a subduction overprint. Lamproites and lamprophyres, which are volcanic rocks resulting from the melting of enriched mantle, are notably nitrogen-rich (tens of parts per million) (Jia *et al.*, 2003), suggesting that such plume events could potentially liberate large amounts of nitrogen into the atmosphere. Nitrogen could also have been liberated by plumes that sampled the lower mantle, which according to some estimates may be nitrogen-rich (Johnson and Goldblatt, 2015). However, both the nitrogen concentration of the lower mantle and the transport pathways of material from such great depth (>660 km) are highly uncertain, making this mechanism difficult to evaluate. Another complication in predicting the effect of superplumes in deep time comes from the possibility that the redox state of magmas may have increased over time, and under more reducing conditions magmatic nitrogen may have been less volatile (Libourel *et al.*, 2003; Kadik *et al.*, 2011; Roskosz *et al.*, 2013; Mikhail and Sverjensky, 2014).

3.3.3. Planetary resurfacing. If superplume events are extended to a planetary scale, as is suggested to have happened on Venus, even more nitrogen could be released. The area of the Siberian traps, to continue the above example, is $2.5 \cdot 10^6$ km^2, or about 1/200th of the surface of Earth. Multiplying the above estimate for nitrogen released during Siberian Trap volcanism by 200 yields a nitrogen output of $2 \cdot 10^{20}$ kg, or $\sim$50 PAN. Again, we note that this is a highly speculative estimate, but it does suggest the possibility of substantial additions of nitrogen to the atmosphere via large-scale volcanism on other planetary bodies that contain substantial amounts of nitrogen in the crust. Overall, catastrophic events could have more marked effects on planets where the crust is nitrogen-enriched, which, as noted above (Section 3.1.2, 3.2.2), is more likely to be the case on planets with a large biosphere that transfers atmospheric nitrogen to crustal repositories.

4. Discussion

4.1. The evolution of atmospheric pN_2 on Earth

Although many parameters in the global biogeochemical nitrogen cycle are uncertain and potential reconfigurations of Earth's interior are not taken into consideration for lack of quantitative constraints (Mikhail and Sverjensky, 2014), our results allow us to draw several broad conclusions under the assumption of persistent tectonic cycling through Earth's history, as follows:

(**1**) The results from our base model (Fig. 2a), where nitrogen burial is held constant through time while oxidative weathering follows atmospheric pO_2, show that the oxygenation of the atmosphere alone could probably not have caused the large swings in atmospheric pN_2 that were suggested by Som *et al.* (2016). Changes in the atmospheric nitrogen reservoir by more than $\sim$0.1 PAN most probably require a change in nitrogen burial over time.

(**2**) Variations in nitrogen burial by up to a factor of 2.9, as inferred from the record of relative organic carbon burial (f_{org}), are insufficient to cause significant swings of more than $\sim$0.2 PAN in atmospheric N_2 (Fig. 2b). Even if we use f_{org} values from the upper end of the uncertainty range (Krissansen-Totton *et al.*, 2015), the atmospheric N_2 reservoir does not drop by more than 0.3 PAN. If f_{org} was smaller than assumed, due to a greater proportion of carbonate formation in oceanic crust or within sediments (Bjerrum and Canfield, 2004; Schrag *et al.*, 2013), this variable would have even less effect on atmospheric N_2. To reach atmospheric pressures of less than 0.5 bar at 2.7 Ga (Som *et al.*, 2016), while maintaining pressures of 0.5–1.1 bar N_2 at 3.5 Ga (Marty *et al.*, 2013), nitrogen burial must have been markedly higher in the earlier Archean than it is today. There are three possible scenarios to increase nitrogen burial: (i) subduction was more efficient than it is today, and metamorphic devolatilization was suppressed; (ii) nitrogen was buried preferentially relative to carbon; (iii) the absolute organic carbon burial flux was much higher, and with it the burial of carbonate, such that f_{org} did not change. It is conceivable that subduction was faster in the Archean (option i), but our sensitivity tests (Section S3) show that shortening the residence time of nitrogen in pelagic sediments by a factor of 2 has minimal effects on the atmospheric reservoir (<0.01 PAN), because the bulk of sedimentary nitrogen is recycled via metamorphism. Metamorphic devolatilization may have been enhanced in the Archean when the geothermal gradient was perhaps somewhat higher than today (Condie and Korenaga, 2010; Cartigny and Marty, 2013), but variations in this parameter also have minimal influence on the output of our model (Section S3). The effects of more rapid subduction and enhanced devolatilization may have more or less canceled each other without a net increase of nitrogen drawdown.

Preferential nitrogen burial (option ii) could potentially occur through adsorption of NH_4^+ onto clay minerals. Boatman and Murray (1982) experimentally derived a relationship between the amount of NH_4^+ adsorbed on clay and the dissolved NH_4^+ concentration in solution. For a doubling of the total nitrogen burial flux, the adsorbed concentration would have to match the concentration of organic nitrogen. Shale samples of sub-greenschist metamorphic grade typically have nitrogen concentrations in the range of 100–1000 ppm with C/N ratios around 40, suggesting that most nitrogen is derived from organics (Stüeken *et al.*, 2016). To achieve this concentration through NH_4^+ adsorption alone would require a dissolved NH_4^+ concentration of 3–30 m*M*, which is 30–300 times higher than the NH_4^+ concentration of the modern Black Sea ($\sim 100\,\mu M$, Brewer and Murray, 1973) and 100–1000 higher than modern marine NO_3^- levels ($\sim 30\,\mu M$, Sverdrup *et al.*, 1942). Such high ammonium abundances are also inconsistent with the nitrogen isotope record, which suggests that N-limited ecosystems dominated by biological N_2 fixation were initiated in the Mesoarchean at 3.2 Ga (Stüeken *et al.*, 2015) and persisted until the GOE at $\sim$2.35 Ga (Stüeken *et al.*, 2016). A large reservoir of dissolved NH_4^+ should have resulted in isotopic fractionations of up to 27‰ associated with partial NH_4^+ assimilation into biomass (Hoch *et al.*, 1992; Pennock *et al.*, 1996), which is not observed. Moreover, due to the extreme energetic cost of splitting the N≡N triple bond, nitrogen fixation should have been suppressed rather than expressed where ammonium was readily available as a nutrient. Enhanced nitrogen burial through adsorption is further inconsistent with the record of C/N ratios, because significant addition of adsorbed NH_4^+ would require consistently lower C/N ratios in the earlier Precambrian, which is opposite to observations; C/N ratios tend to increase with increasing age due to preferential nitrogen loss during low-grade metamorphism (Stüeken *et al.*, 2016). NH_4^+ adsorption to clays likely did occur during diagenesis, where NH_4^+ in pore waters can become enriched to several millimolar by degradation of organic matter (*e.g.*, Rosenfeld, 1979; Boudreau and Canfield, 1988), but in that case the adsorbed nitrogen is simply returned to the sediment from which it was derived and does not lead to excess nitrogen burial. Enhanced NH_4^+ adsorption in the Archean ocean is therefore unlikely to have caused a drawdown in atmospheric N_2. Instead, we find it more likely that absolute organic carbon burial, and with it organic nitrogen burial, was significantly higher (option iii).

(**3**) Enhanced volcanic CO_2 outgassing in the earlier Precambrian could explain greater nitrogen burial if accompanied by increased burial of both organic matter and carbonate. The observed constancy of f_{org} could have been maintained through carbonatization of oceanic crust as a large carbonate sink (Nakamura and Kato, 2004). Organic matter burial was likely concentrated under anoxic waters along continental margins where sedimentation rates were high. Such an enhanced biomass burial flux would have led to an increase in nitrogen burial and can thus explain the observation of low Neoarchean pN_2 (Fig. 2c). Following the formulation of Canfield (2004) for a higher heatflow and proportionally higher volcanic fluxes in deep time, this scenario increases the nitrogen burial flux by 40–80% (depending on the exact age) relative to our early Paleozoic base value, or 3.4–1.9 times above the f_{org} factor alone, throughout most of the Archean. We note that the assumption of a higher Archean CO_2 flux (Canfield, 2004; Zahnle *et al.*, 2006) has been challenged by studies arguing for a gradual increase in CO_2 outgassing from the Archean into the Proterozoic, concurrent with late continental growth (Holland, 2009; Lee *et al.*, 2016). However, if volcanic CO_2 emissions were lower in the Archean than they are today, absolute carbon burial would have been lower and with it the burial of nitrogen. Low Archean CO_2 fluxes would only be compatible with high nitrogen burial if f_{org} had been much higher than generally assumed. A high Archean CO_2 flux thus remains the most plausible mechanism in our model to explain a decline in pN_2 from 0.5–1.1 bar at 3.5 Ga to <0.5 bar at 2.7 Ga, as suggested by paleobarometers (Marty *et al.*, 2013; Som *et al.*, 2016). We will therefore proceed with this assumption, noting that the Archean CO_2 flux requires additional constraints to derive a more accurate trajectory for pN_2.

We further note that a higher absolute burial flux of organic carbon would constitute a source of oxygen equivalents that would have needed to be balanced by reductants to maintain anoxic surface conditions in the Archean (Kasting, 2013). Proposed fluxes of possible reductants (H_2, CO, H_2S, Fe^{2+}) range over an order of magnitude (reviewed by Zahnle *et al.*, 2006; Holland, 2009) and could therefore plausibly cover the effect of carbon burial. Reductant fluxes may indeed have been higher than previously suggested during the earlier Archean if new evidence for a secular increase in the redox state of Earth's mantle is taken into account (Nicklas *et al.*, 2015). A 2- to 4-fold higher carbon burial flux does therefore not necessarily violate redox balance models.

If we calibrate our model with the results of Som *et al.* (2016), who inferred an atmospheric pressure of <0.5 bar from the relative sizes of vesicles in basalt flows, then the lower part of our uncertainty range in Fig. 2c is more likely to be correct than the upper part. In this case, our model predicts the lowest atmospheric pressure in the Neoarchean and two stepwise increases across the Paleoproterozoic and Neoproterozoic oxidation events, when oxidative weathering progressively shortens the residence time of nitrogen in continental sediments and crust. Our prediction of $\sim$0.6 PAN (=0.47 bar N_2) in the Mesoproterozoic is testable with further analyses of vesicle sizes in Proterozoic lava flows.

(**4**) The effect of superplumes is difficult to assess; they could have led to either more rapid nitrogen recycling through crustal melting or slightly enhanced nitrogen drawdown through carbon burial. The balance may further depend on the redox state of magmas, which may have changed over time in favor of progressively more N_2 degassing (Mikhail and Sverjensky, 2014). Overall, reconfigurations of the deep Earth are currently poorly constrained, but these could potentially have significant effects, beyond the scope of our model.

4.2. Climatic effects of atmospheric pN_2 *changes in the Archean*

Significant changes of >0.1 PAN in our modeled atmospheric N_2 abundances occur over several hundred million-year time scales (Fig. 2c, 2d). Although atmospheric pressure affects the greenhouse efficiency of other atmospheric gases like CO_2 through pressure broadening (Goldblatt *et al.*, 2009) and can therefore theoretically cause changes in surface temperature, these time scales are so long that any resulting temperature change could be balanced by the carbonate-silicate feedback cycle, which has a response time on the order of a few hundred thousand years (Sundquist, 1991). As pN_2 declines, greenhouse warming decreases, causing the planet to cool. However, with lower temperatures, silicate weathering by carbonic acid slows down, which lowers the sink flux of atmospheric CO_2 from the atmosphere (Walker *et al.*, 1981). CO_2 would thus build up and balance the temperature change caused by the drop in pN_2.

Table 1 shows the required response in pCO_2 to our calculated drop in pN_2 in the Archean. These calculations also take into account the increasing solar luminosity, which warms the planet and therefore leads to a steady decrease in pCO_2. In sum, the effect of rising solar luminosity overpowers the effect of declining pN_2 from 3.5 to 2.7 Ga in our nominal model scenario (Fig. 2c); hence pCO_2 would have needed to decrease to maintain a stable surface temperature of 278 K. If pCO_2 did not respond, then surface temperature would increase by about 4 degrees over this time interval due to the increase in solar luminosity, despite the drop in pN_2. It is only in cases of extreme nitrogen burial, that is, at the lower limit of our uncertainty interval in the model with an additional superplume (Fig. 2d, excluding potential effects of crustal melting), that the decline in pN_2 would cause surface temperature to drop by around 7.5 degrees. This drop could have been counterbalanced by a 3- to 5-fold increase in pCO_2. We note that all our calculated values for pCO_2 fall within, or very close to, the range of late Archean CO_2 pressures inferred from the rock record (0.003–0.15 bar at 2.5 Ga and 0.004–0.75 bar around 2.7 Ga, Sheldon, 2006; Driese *et al.*, 2011; Kanzaki and Murakami, 2015). Although these estimates vary widely, this agreement suggests that our model results are not unrealistic. Overall, plausible changes in atmospheric pN_2 as inferred from our model are unlikely to have resulted in massive climatic perturbations. [We note that a requirement for globally averaged temperatures approaching modern values ($\sim$288 K) or higher throughout the Archean would be hard to reconcile with the most restrictive constraints on pCO_2 from paleosols even without the climatic impact of falling pN_2, which is the well-known Faint Young Sun Paradox. For all but our most extreme scenarios, falling pN_2 would only negligibly exacerbate this problem.]

4.3. N_2 *in extraterrestrial atmospheres*

Geological and potential biological processes on other planets may differ markedly from those on Earth, as might the initial volatile inventory. Our results can therefore only provide qualitative trends, but they may nevertheless serve as useful guidelines in evaluating measurements of atmospheric pN_2 in exoplanetary atmospheres (Schwieterman *et al.*, 2015b). At the very least, our approach allows us to isolate selected variables that have the potential to play a major role in the evolution of a planet's nitrogen cycle.

Most importantly, nitrogen burial under completely abiotic and anoxic conditions on an Earth-like planet within the habitable zone is likely to be trivial compared to mantle degassing; hence an uninhabited Earth-like planet with a significant nitrogen inventory is unlikely to ever show low atmospheric N_2 pressures (Fig. 3a). This conclusion may be violated in a few cases, as follows:

(a) On young, very hot (>1000 K), reducing planets, N_2 may be rapidly reduced to NH_3 and dissolved in a magma ocean (Wordsworth, 2016). This scenario could probably be ruled out by inferring the planetary temperature through measurements of infrared emission, examination of the planet's atmospheric scale height to determine H_2 abundance, and/or observations of the host star to provide an estimate of the planet's age.
(b) Atmospheric pN_2 may be permanently low on planets that have lost their atmosphere by erosion and where the outgassing rate is at least an order of magnitude lower so that the atmosphere cannot be replaced (*e.g.*, modern Mars). In this case, however, the abundance of other atmospheric gases would also be very low, and the planet's propensity to lose its atmosphere could be inferred from direct or indirect measurements of its mass and radius and therefore its surface gravity.
(c) Nitrogen burial could be more effective if abiotic N_2 fixation by volcanism, lightning, or impacts (Kasting and Walker, 1981; Kasting, 1990; Navarro-González *et al.*, 1998; Mather *et al.*, 2004) is at least an order of magnitude higher than estimated for early Earth. If the pH of the ocean on such a planet is significantly higher than 5, then even larger fixation rates would be required, because otherwise fixed NH_4^+ (produced after conversion of NO_3^- to NH_4^+ via hydrothermal reduction) (Brandes *et al.*, 1998) would be returned to the atmosphere as NH_3 gas instead of adsorbing onto mineral surfaces (Stüeken, 2016). NH_3 gas quickly dissociates back to N_2 under UV light (Kuhn and Atreya, 1979). So far, a theoretical basis for unusually high extraterrestrial lightning rates is lacking. Enhanced volcanic activity may be detectable remotely through time-dependent observations of sulfate aerosols through transmission spectroscopy (Misra *et al.*, 2015).
(d) Planets may have had a large compositional deficit of nitrogen after the initial period of accretion and enhanced atmospheric erosion by stellar UV light (Lichtenegger *et al.*, 2010; Wordsworth and Pierrehumbert, 2014). This scenario may be detectable through the abundance of other volatiles in the planet's atmosphere or measurements of the nitrogen abundance in the host star (*e.g.*, Brewer *et al.*, 2016).
(e) Planets with a markedly lower oxygen fugacity in their mantle compared to that of Earth may not degas N_2, because mantle nitrogen may be stable as NH_3 and thus less volatile (Mikhail and Sverjensky, 2014; Li *et al.*, 2015). But such planets may be discernable by the presence of CO rather than CO_2 in their atmospheres.

For planets that do not fall within the habitable zone, and thus are not covered by our model results, other scenarios could apply. For example, planets that are closer to the host star than the habitable zone that lack a surface ocean, such as Venus, would show insignificant nitrogen burial; hence atmospheric N_2 would increase as the mantle degasses. This effect would be enhanced on planets with a high oxygen fugacity where N_2 outgassing is favored over NH_3 retention, as proposed for early Venus (Wordsworth, 2016). Planets far beyond the habitable zone may have low atmospheric pN_2 if temperatures drop low enough for N_2 to become liquid or solid, such as on modern Pluto and possibly ancient Titan (McKay *et al.*, 1993; Lorenz *et al.*, 1997). Hence, pN_2 can fluctuate abiotically in such extreme cases, but for Earth-like planets within the habitable zone as considered in our model, abiotic N_2 drawdown is much less likely.

A biosphere on a completely anoxic Earth-like planet can potentially have substantial effects on atmospheric N_2 (Fig. 3b). A nitrogen burial flux equivalent to a few percent of modern biological N_2 fixation rates (without oxidative remineralization) may be sufficient to deplete the atmosphere of N_2 if mantle outgassing rates are comparable to those of Earth. In the absence of oxidative weathering, the only steady return fluxes of buried nitrogen back to the atmosphere would be metamorphism, volcanism, and mantle outgassing, and possibly catastrophic events (Section 3.3.2). It is important to note, however, that burial rates may be significantly different on planets that lack a surface reservoir equivalent to continental crust on Earth (Fig. 3d), which is able to take up and release atmospheric N_2 on hundred-million-year timescales.

Overall, our results strengthen the conclusion that the simultaneous presence of significant amounts of *both* N_2 and O_2 may be a biosignature and indicative of a biosphere with oxygenic photosynthesis (Schwieterman *et al.*, 2015b; Krissansen-Totton *et al.*, 2016) (Fig. 4). As shown above, a large anaerobic biosphere that never ''invents'' oxygenic photosynthesis can draw down N_2 to relatively low levels. Hence, both O_2 and N_2 would be low. Atmospheric erosion and the possibility of an unusually low mantle fugacity can be evaluated independently in such a scenario (*e.g.*, Mars). On a completely abiotic planet orbiting in the habitable zone of a Sun-like star, O_2 can build up abiotically, but probably only under the condition that non-condensible gases (including N_2) are present in low amounts (Wordsworth and Pierrehumbert, 2014). According to this model, water from a surface ocean would be able to enter the upper atmosphere, where it would be photolyzed by UV, causing the H to escape and O to build up after surface sinks for oxidants are depleted. In this case, N_2 must start and remain low; otherwise the process is halted. Hence, high levels of abiotic O_2 would not coexist with a thick N_2 atmosphere. [Though note the likelihood that abiotic O_2 may be substantially higher for

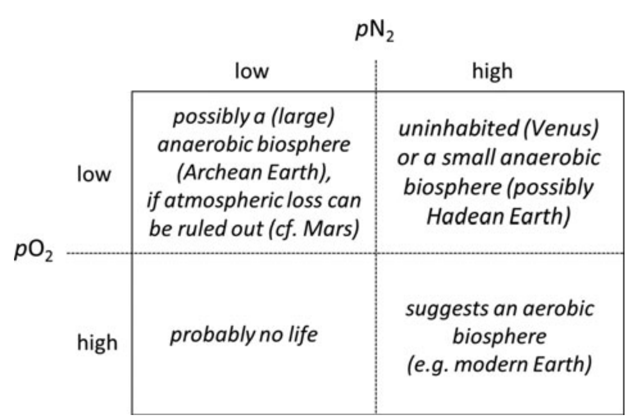

FIG. 4. Plausible interpretations of observed N_2 and O_2 abundances in exoplanetary atmospheres. Quantitative constraints on cutoffs for ''low'' and ''high'' abundances would need to be evaluated based on measurements of other gases and comparisons to other planets in the observed system.

planets orbiting M dwarf stars due to other mechanisms not applicable to solar-type host stars (*e.g.*, Harman *et al.*, 2015; Luger and Barnes, 2015)]. A high-O_2-low-N_2 scenario is difficult to create biologically given the strong tendency of oxidative weathering and increasing oxygen fugacity in the mantle to release N_2 to the atmosphere. An inhabited planet whose biosphere invents oxygenic photosynthesis could eventually transition to oxidative weathering, thereby initiating rapid recycling of buried nitrogen from continental crust as on early Earth (*e.g.*, Fig. 2c). This is thus perhaps the only case where both N_2 and O_2 reach high relative abundances in the atmosphere. In summary, (1) a planet with high pN_2 and no O_2 probably has either no biosphere (*e.g.*, Venus) or a very small and/or young biosphere (*e.g.*, first life on the Hadean Earth) that is incapable of transferring large quantities of nitrogen to the crust; (2) a planet with O_2 but no N_2 may be uninhabited; (3) a planet with neither O_2 nor high (modern) abundances of N_2 may host an anaerobic biosphere as exemplified by Archean Earth, provided that atmospheric erosion can be ruled out (*cf.* Mars); and (4) a planet with both significant N_2 and O_2 suggests the presence of a biosphere powered at least in part by oxygenic photosynthesis as on modern Earth. Low total N_2 on an anoxic planet (case 3) may be a weak biosignature, which could be confirmed through the detection of other biosignature gases or surface features (*e.g.*, Des Marais *et al.*, 2002; Pilcher, 2003; Domagal-Goldman *et al.*, 2011; Schwieterman *et al.*, 2015a).

5. Conclusion

The wide range of uncertainties in all our models, in particular about anything related to possible reconfigurations of Earth's mantle (Mikhail and Sverjensky, 2014), prohibits firm conclusions. Nevertheless, our results allow us to isolate a few key parameters for the evolution of a planet's nitrogen cycle and to formulate hypotheses about the evolution of atmospheric N_2 reservoirs on Earth and other planets. Some of these hypotheses may be testable with more constraints on nitrogen fluxes and with additional measurements of geological proxies for atmospheric pressure (Som *et al.*, 2012; Marty *et al.*, 2013; Glotzbach and Brandes, 2014; Kite *et al.*, 2014; Som *et al.*, 2016) (see Kavanagh and Goldblatt, 2015, for possible complications).

To first order, our results suggest that the greatest variability in atmospheric pN_2 over the history of a planet can be achieved if the planet is inhabited, if biomass burial is highly variable, and/or if it experiences oxygenation events or large-scale crustal melting. Other abiotic scenarios could be envisioned that could potentially lead to pN_2 fluctuations, such as N_2 freeze-out or atmospheric loss, but many of these cases would likely be discernable through other observations, in particular the orbit of the planet and the abundances of other gases. On an inhabited planet, variation in biomass burial can result from changes in the supply of metabolic substrates, including CO_2 (as on Earth, Fig. 2c, 2d) and N_2 (as in potential exoplanets, Fig. 3b). In the case of Earth, enhanced biomass burial in the Archean, followed by a stepwise shortening of the crustal residence time across the Paleoproterozoic and Neoproterozoic increases in oxidative weathering, could explain the drawdown and recovery of atmospheric N_2 inferred from abundances of N_2 in fluid inclusions at 3.5 Ga (Marty *et al.*, 2013) and the size distribution of basaltic amygdales at 2.7 Ga (Som *et al.*, 2016). We note that there is no independent evidence of enhanced burial of both organic carbon and carbonate in the Archean, because total organic carbon (TOC) and carbonate contents of Archean sedimentary rocks are not known to be particularly high. This discrepancy may suggest that large amounts of carbon-rich sediments and carbonated basalts have been subducted and lost. If one were to reject our hypothesis of enhanced nitrogen drawdown into continental crust as a temporary reservoir, then another alternative possibility for explaining a low Neoarchean N_2 pressure (Som *et al.*, 2016) would be a much lower initial pN_2 value in the early Archean, followed by a marked increase in mantle degassing at some time between the Neoarchean and the modern. A test with our "F_{org}" model suggests that such a trajectory could be achieved if the mantle degassing rate were an order of magnitude higher throughout Earth's history than thought (Busigny *et al.*, 2011). However, this scenario would be inconsistent with proposed N_2 pressures of 0.5–1.1 bar at 3.5 Ga (Marty *et al.*, 2013). There is also no evidence for a major transition in the style or rate of mantle outgassing. But if such a transition occurred, it could conceivably be related to proposed changes in the mantle's redox state (Mikhail and Sverjensky, 2014; Nicklas *et al.*, 2015; Aulbach and Stagno, 2016). Further research is needed to evaluate this possibility.

Lastly, our results may have some practical implications for observations of extrasolar planets. Despite all the uncertainties in our models, our results suggest that an anaerobic biosphere can—under Earth-like geological conditions—remove significant amounts of N_2 from the atmosphere. If multiple terrestrial planets around another star started out with similar volatile contents, but one of them has a significantly lower atmospheric N_2 abundance, then this may potentially serve as a biosignature. Measurements of other gases may be necessary to rule out atmospheric erosion as on Mars. In contrast, a planet with an oxygenic biosphere that stimulates oxidative weathering could maintain an atmosphere rich in both N_2 and O_2, similar to post-Archean Earth. Our results thus support the idea that the combination of N_2 and O_2 in an exoplanetary atmosphere may be a signature of a biosphere that is capable of oxygenic photosynthesis (Wordsworth and Pierrehumbert, 2014; Schwieterman *et al.*, 2015b; Krissansen-Totton *et al.*, 2016).

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No competing financial interests exist.

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Address correspondence to:
E.E. Stüeken
Department of Earth and Space Sciences
University of Washington
Seattle, WA 98195

E-mail: evast@uw.edu

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Abbreviations Used

GOE = Great Oxidation Event
NOE = Neoproterozoic Oxidation Event
PAN = present atmospheric nitrogen
TOC = total organic carbon