This section focuses on describing process functions and fluxes related to the nitrogen cycle in the Precambrian ocean. For detailed information on other relevant processes within the Earth system, please refer to the original literature on the Lewis model. Further insights into the expansion of the iron cycle in the Lewis model and its integration with geological records can be found in the relevant publications.

**Hydrodynamic Nitrogen Transport Processes**

The transport of NO₃⁻ and NH₄⁺ between different oceanic boxes is calculated based on hydrodynamic principles. Taking the transport of NO₃⁻ in the surface ocean as an example, the flux is assumed are positively correlated with the concentration of the substance within the respective box.

*NO3\_D\_S = NO3\_Dconc* • *Water\_D\_S* (1)

*NO3\_S\_DP = NO3\_Sconc* • *Water\_S\_DP* (2)

*NO3\_DP\_S = NO3\_DPconc* • *Water\_DP\_S* (3)

*NO3\_D\_S* and *Water\_D\_S* represent the transport fluxes of NO3⁻ and water from the distal shelf zone to the surface ocean box. *\_S\_DP* denotes the transport from the surface ocean box to the deep ocean box, while *\_DP\_S* represents the upwelling transport from the deep ocean box back to the surface ocean. *NO3\_Dconc* refers to the NO3⁻ concentration in the distal shelf zone, while *\_S* and *\_DP* correspond to the NO3⁻ concentrations in the surface ocean and deep ocean, respectively.

##### **Quantification of Marine Organic Nitrogen Production and Mineralization**

##### The total production of organic nitrogen in the ocean can be estimated based on the modeled production of organic phosphorus, using the Redfield ratio (106C:16N:1P) for conversion. Both NO₃⁻ and NH₄⁺ can be assimilated by microorganisms to form organic nitrogen, and we assume that their contributions to organic nitrogen production are positively correlated with their bioavailability. Similarly, the mineralization of organic nitrogen can be quantified by converting the modeled mineralization of organic phosphorus according to the Redfield ratio.

*N\_PP = P\_PP\_P* • *pars.Redfield\_NP* (4)

*NO3\_PP = (NO3 / TN)* • *N\_PP* (5)

*NH4\_PP = (NH4 / TN)* • *N\_PP* (6)

##### *P\_PP\_P* represents the production of organic phosphorus, while *pars.Redfield\_NP* corresponds to the Redfield ratio of 16:1. Consequently, *N\_PP* represents the production of organic nitrogen. *NO₃\_PP* and *NH₄\_PP* denote the assimilation of NO₃⁻ and NH₄⁺, respectively, into organic nitrogen. TN represents the total pool of NO₃⁻ and NH₄⁺ combined. The fraction *NO₃ / TN* indicates the proportion of the total available nitrogen pool contributed by NO₃⁻, which is assumed to be linearly related to the amount of organic nitrogen produced from NO₃⁻ assimilation; the same applies to NH₄⁺ assimilation. These calculations take place within the proximal shelf box, distal shelf box, and surface ocean box. Due to light limitations, the deep ocean box is assumed to have no primary production.

*PON\_Min = OP\_Min* • *pars.Redfield\_NP* (7)

*OP\_Min* represents the mineralization of organic phosphorus, while *PON\_Min* refers to the mineralization of organic nitrogen. This process occurs in the proximal shelf box, distal shelf box, surface ocean box, and deep ocean box.

**Terrestrial Nitrogen Input, Nitrogen Fixation, Nitrification, and Denitrification Fluxes**

Given the minimal nitrogen contribution from rock weathering, terrestrial nitrogen input in the Precambrian ocean, similar to carbon, is primarily controlled by the intensity of oxidative weathering and the extent of continental exposure, following a linear relationship.

*River\_NO3 = k\_River\_NO3* • *Foxidw* • *EXPOSED* (8)

*River\_NH4 = k\_River\_NH4* • *Foxidw* • *EXPOSED* (9)

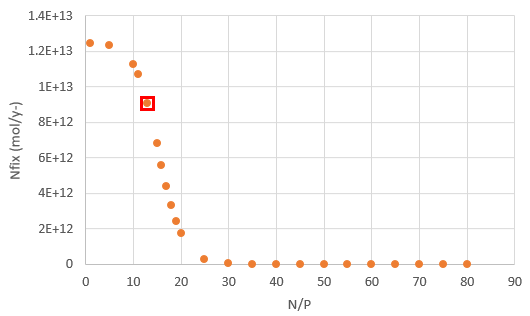
*k\_River\_NO3* and *k\_River\_NH4* represent the modern terrestrial input fluxes of NO₃⁻ and NH₄⁺, respectively. *Foxidw* denotes the normalized amount of oxidative weathering at present day. *EXPOSED* represents the extent of continental exposure relative to the present.

The nitrogen fixation process is determined by nitrogen and phosphorus availability. We assess nitrogen or phosphorus limitation based on the Redfield ratio. Simply put, when the N:P ratio is below the Redfield ratio of 16, nitrogen is relatively scarce compared to phosphorus, indicating nitrogen limitation. Conversely, when the ratio exceeds 16, nitrogen is more abundant relative to phosphorus.

Previous studies have shown that high nitrogen conditions significantly reduce nitrogen fixation efficiency [[104](#_ENREF_104)，[105](#_ENREF_105)]. However, nitrogen fixation is also influenced by other factors such as light availability and phosphate concentration [[106](#_ENREF_106)]. Therefore, we model nitrogen fixation as a nonlinear function of the N:P ratio:

*NH4\_Nfix = k\_Nfix / (0.8 + exp(0.4*• *(TN / SRP - 16)))* (10)

*k\_Nfix* represents the nitrogen fixation flux in the modern ocean. The offset constant is set to 0.8, while the sensitivity constant for nitrogen fixation in response to changes in the N:P ratio is 0.4. SRP denotes the flux of dissolved phosphate. This approach not only allows for the simulation of modern nitrogen fixation fluxes but also yields results consistent with other models. The process primarily occurs in the proximal shelf, distal shelf, and surface ocean.



The nitrification process is controlled by oxygen availability and NH₄⁺ concentration, following a positive linear relationship, defined as:

*NO3\_Nitri = k\_Nitri • Norm\_O2 • Norm\_NH4* (11)

*k\_Nitri* represents the nitrification flux in the modern ocean. *Norm\_O2* denotes the normalized oxygen concentration relative to present day. Similarly, *Norm\_NH4* denotes the normalized NH₄⁺ concentration relative to present day. This process occurs in the proximal shelf, distal shelf, surface ocean, and deep ocean.

Denitrification flux is also controlled by redox conditions and the evolution of the NO₃⁻ reservoir. Over long timescales, it is negatively correlated with oxygen concentration and positively correlated with NO₃⁻ concentration. Notably, in the modern ocean, approximately 30% of denitrification occurs in the water column, while the remaining 70% takes place in sediments. These two forms of denitrification differ in their controlling factors and isotopic fractionation effects. Due to strong mixing in the water column, denitrification is influenced by the nitrification rate. In contrast, the stratified nature of sediments separates the zones where nitrification and denitrification occur, weakening their direct coupling. Therefore, we define the process as follows:

*Denit\_water = 0.3• k\_denit • Norm\_Nitr • Norm\_NO3• (1 - Norm\_O2)* (12)

*Denit\_sediment = 0.7* • *k\_denit* • *Norm\_NO3• (1+(1 - Norm\_O2))* (13)

*k\_denit* represents the denitrification flux in the modern ocean, while *\_water* and *\_sediment* denote denitrification occurring in the water column and sediments, respectively. *Norm\_Nitr* denotes the normalized nitrification flux relative to present-day values, *Norm\_NO3* represents the normalized NO₃⁻ concentration, and *Norm\_O2* indicates the normalized oxygen concentration.

It is important to note that in this model, the surface ocean box primarily represents the photic zone, where denitrification does not occur. Instead, the process takes place mainly in the proximal shelf, distal shelf, and deep ocean.

**Quantitative Modeling of Total Nitrogen and Nitrogen Isotope δ¹⁵N**

In the box model, total oceanic nitrogen is calculated based on the balance between nitrogen input and output processes. In our system, inputs include terrestrial nitrogen influx and atmospheric nitrogen fixation, while outputs consist of denitrification in the water column and sediments, as well as nitrogen burial. Since the nitrification process primarily converts NH₄⁺ to NO₃⁻, it does not affect the total nitrogen budget. The nitrogen burial process is defined as the total organic nitrogen production minus the total organic nitrogen mineralization. Therefore, total nitrogen can be calculated as follows:

*N\_total = River\_NH4 + River\_NO3 + total\_Nfix - total\_water\_denit -total\_sediment\_denit - total\_bury* (14)

*total\_Nfix* represents the total nitrogen fixation flux, *total\_water\_denit* denotes the total denitrification flux in the water column, *total\_sediment\_denit* corresponds to the total denitrification flux in sediments, and *total\_bury* represents the total nitrogen burial flux.

The calculation of δ¹⁵N follows the principle of isotopic mass balance, where the total isotopic composition of the system is determined by the weighted average of the δ¹⁵N values from all nitrogen inputs and outputs, based on their respective nitrogen fluxes.

For terrestrial nitrogen inputs, the δ¹⁵N values of NO₃⁻ and NH₄⁺ differ from those in the marine system, with modern values set at 5‰, respectively. Since nitrogen fixation exhibits negligible isotopic fractionation (~0‰), its contribution to the system’s overall δ¹⁵N value is considered minimal. Denitrification in sediments typically occurs at a faster rate and is associated with lower nitrogen fractionation, resulting in a weaker influence on δ¹⁵N. In contrast, water column denitrification exhibits significant nitrogen isotopic fractionation and is one of the primary contributors to the positive δ¹⁵N shifts in the system. Therefore, the calculation can be set as follows:

*δ15N = (River\_NH4*•*5 + River\_NO3*•*5 + total\_marine\_Nfix* • *δ15N - total\_water\_denit* • (*δ15N-15) - total\_sediment\_denit* • *δ15N - total \_bury* • *δ15N) / N\_total* (15)

**Control of Primary Production by Available Nitrogen**

In the original model, primary production is primarily limited by phosphorus availability, expressed as:

*PP\_P = k\_Photo • Norm\_SRP* (16)

*PP\_P* represents the production of organic carbon, while *k\_Photo* denotes the organic carbon production rate in the modern ocean. *Norm\_SRP* denotes the normalized phosphate concentration relative to present-day levels*.*

However, when nitrogen also acts as a limiting nutrient affecting primary production, the overall production rate will be constrained by the scarcer of the two nutrients, nitrogen or phosphorus. Therefore, we modify the equation as follows: *transition\_range = 0.1 • (TN\_conc / 16)*

*If SRP\_conc < (TN\_conc / 16 - transition\_range)*

*PP\_P = k\_Photo • Norm\_SRP*

*Elseif SRP\_Pconc > (TN\_conc / 16 + transition\_range)*

*PP\_P = k\_Photo • Norm\_TN*

*Else*

*proportion\_P = ((TN\_conc / 16) + transition\_range - SRP\_conc) / (2 • transition\_range);*

*proportion\_N = 1 - proportion\_P*

*PP\_P = k\_Photo • (proportion\_P • Norm\_SRP + proportion\_N • Norm\_TN)* (17)

*TN\_conc* represents the concentration of available nitrogen (NO₃⁻ + NH₄⁺), while

*Norm\_TN* represents the normalized total nitrogen availability relative to present-day ocean levels*.* In the model, a 10% nitrogen-phosphorus transition range (transition\_range) is implemented to ensure a smooth shift between nitrogen- and phosphorus-limited primary production states, preventing abrupt changes. When the relative concentrations fall within this 10% transition range, primary production is co-limited by both nitrogen and phosphorus.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Reservoir | Label | Initial Size | Differential Equation | Source |
| Proximal NO3- | NO3\_P | 1.4e11 |  |  |
| Distal  NO3- | NO3\_D | 5.5e13 |  |  |
| Surface NO3- | NO3\_S | 6.11e14 |  |  |
| Deep ocean NO3- | NO3\_DP | 3.9e16 |  |  |
| Proximal NH4+ | NH4\_P | 1.4e10 |  |  |
| Distal NH4+ | NH4\_D | 7.2e11 |  |  |
| Surface NH4- | NH4\_S | 3.62e12 |  |  |
| Deep ocean NH4- | NH4\_DP | 1.3e13 |  |  |

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Flux | Label | Initial Size | Equation | Source |
| Riverine NO3- input | River\_NO3 | 1.5e12 |  |  |
| Riverine NH4+ input | River\_NH4 | 1e11 |  |  |
| Proximal primary production (N) | N\_PP\_P | 6e12 |  |  |
| Distal primary production (N) | N\_PP\_D | 8.45e13 |  |  |
| Surface primary production (N) | N\_PP\_S | 5.83e14 |  |  |
| Proximal PON mineralisation | PON\_Min\_P | 4.94e12 |  |  |
| Distal PON mineralisation | PON\_Min\_D | 8.07e13 |  |  |
| Surface PON mineralisation | PON\_Min\_S | 5.07e14 |  |  |
| Deep ocean PON mineralisation | PON\_Min\_DP | 8.03e13 |  |  |
| Proximal N fixation | Nfix\_P | 0.1e12 |  |  |
| Distal N fixation | Nfix\_D | 2.3e12 |  |  |
| Surface N fixation | Nfix\_S | 10e12 |  |  |
| Proximal nitrification | Nitri\_P | 4.52e12 |  |  |
| Distal nitrification | Nitri\_D | 8.19e13 |  |  |
| Surface nitrification | Nitri\_S | 5.15e14 |  |  |
| Deep ocean nitrification | Nitri\_DP | 8.14e13 |  |  |
| Proximal water column denitrification | Denit\_water\_P | 1.35e11 |  |  |
| Proximal sediment denitrification | Denit\_sed\_P | 3.15e11 |  |  |
| Distal water column denitrification | Denit\_water\_D | 1.11e12 |  |  |
| Distal sediment denitrification | Denit\_sed\_D | 2.59e12 |  |  |
| Deep ocean water column denitrification | Denit\_water\_DP | 2.31e12 |  |  |
| Deep ocean sediment denitrification | Denit\_sed\_DP | 5.39e12 |  |  |
| Total N | N\_total | 4.13e16 |  |  |
| Total N isotope | N\_15N | 4.84 |  |  |