A seasonal model of nitrogen isotopes in the ice age Antarctic Zone: Support for weakening of the Southern Ocean upper overturning cell

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Supplement S1: Model Equations

Fluxes of ^{14}N and ^{15}N between nitrogen reservoirs are described with differential equations implemented in MATLAB. For non-fractionating physical processes, such as mixing, N fluxes are calculated as a concentration-weighted volume balance. For fractionating processes, the flux of ^{15}N depends on the flux of ^{14}N, the concentrations of substrate ^{14}N and ^{15}N, and the isotope effect of the process. Hayes (2004) provides the solution for heavy isotope flux in the case where the isotope effect, the flux of the light isotope, and the abundance of both reacting isotopes are known. The solution is shown in eq. S1, where ^{14}F and ^{15}F are the fluxes of ^{14}N and ^{15}N, ^{14}A and ^{15}A are the initial abundances of ^{14}N and ^{15}N in the reacting reservoir, and $^{15}\alpha$ is the isotope effect (defined for $(^{15}N/^{14}N)_{product}/(^{15}N/^{14}N)_{reactant}$). This solution accounts for the decreased significance of isotope effects at higher degrees of substrate utilization. For all fractionating processes in the model, the flux of ^{15}N is calculated using eq. S1. Below we present the full model equations for ^{14}N and give the ^{15}N equations in terms of the function ^{15}F as defined in eq. S1. For clarity, the full function $^{15}F[^{15}A, \, ^{14}A, ^{14}F, \, ^{15}\alpha]$ is written with fewer inputs as $^{15}F[^{14}F, \, ^{15}\alpha]$. The fluxes among N reservoirs are mostly first order in concentration, and coefficients are given in Table 1 of the main text. In this case $^{14}F = \kappa *^{14}A$, and ^{15}F simplifies to eq. S2. However, several fluxes are not first-order, including diatom assimilation of NO_3^- and zooplankton assimilation of N. As discussed in the main text, diatom assimilation of $^{14}NO_3^-$ follows a Monod equation. The consumption of N by zooplankton involves a digestive step; a fraction of the diatoms and non-diatom phytoplankton that zooplankton consume are fractionated at -3‰ during digestion before becoming zooplankton biomass, with the remainder exported as fecal pellets. The model begins with surface $[NO_3^-]$ of 5 mmol/m^3 and T_{min} $[NO_3^-]$ of 10 mmol/m^3, both reservoirs with NO_3^- $\delta^{15}N = 4.74‰$.

Symbols:

^{14}A,   Example abundance of ^{14}N in the reacting reservoir

^{15}A,   Example abundance of ^{15}N in the reacting reservoir

^{14}F,   Example flux of ^{14}N to the product reservoir

^{15}F,   Example flux of ^{15}N to the product reservoir

$^{15}\alpha$,   Isotope effect of the example process

$_{Srf}^{14}NO3$, ^{14}NO$_3^-$ in the surface ocean (mmol/m^3)

$_{Srf}^{15}NO3$, ^{15}NO$_3^-$ in the surface ocean (mmol/m^3)

$_{Tmin}^{14}NO3$, ^{14}NO$_3^-$ in the temperature minimum layer (mmol/m^3)

$_{Tmin}^{15}NO3$, ^{15}NO$_3^-$ in the temperature minimum layer (mmol/m^3)

$_{Srf}^{14}NH4$, ^{14}NH$_4^+$ in the surface ocean (mmol/m^3)

$_{Srf}^{15}NH4$, ^{15}NH$_4^+$ in the surface ocean (mmol/m^3)

$_{Tmin}^{14}NH4$, ^{14}NH$_4^+$ in the temperature minimum layer (mmol/m^3)

$_{Tmin}^{15}NH4$, ^{15}NH$_4^+$ in the temperature minimum layer (mmol/m^3)

$_{Srf}^{14}Dtm$, ^{14}N in diatom biomass in the surface ocean (mmol/m^3)

$_{Srf}^{15}Dtm$, ^{15}N in diatom biomass in the surface ocean (mmol/m^3)

$_{Srf}^{14}Fru$, ^{14}N in diatom frustules in the surface ocean (mmol/m^3)

$_{Srf}^{15}Fru$, ^{15}N in diatom frustules in the surface ocean (mmol/m^3)

$_{Srf}^{14}Zoo$, ^{14}N in zooplankton in the surface ocean (mmol/m^3)

$_{Srf}^{15}Zoo$, ^{15}N in zooplankton in the surface ocean (mmol/m^3)

$_{Srf}^{14}Phyto$, ^{14}N in non-diatom phytoplankton in the surface ocean (mmol/m^3)

$_{Srf}^{15}Phyto$, ^{15}N in non-diatom phytoplankton in the surface ocean (mmol/m^3)

^{14}T, ^{14}N addition to diatom biomass + frustule (mmol/m^3/day)

^{15}T, ^{15}N addition to diatom biomass + frustule (mmol/m^3/day)

^{14}B, ^{14}N addition to diatom biomass (mmol/m^3/day)

^{15}B, ^{15}N addition to diatom biomass (mmol/m^3/day)

^{14}Fr, ^{14}N addition to diatom frustule (mmol/m^3/day)

^{15}Fr, ^{15}N addition to diatom frustule (mmol/m^3/day)

R,   Fraction of diatom N in the diatom frustule

$_{Sed}^{14}Dtm$, ^{14}N in exported diatom biomass (mmol/m^2)

$_{Sed}^{15}Dtm$, ^{15}N in exported diatom biomass (mmol/m^2)

$_{Sed}^{14}Fru$, ^{14}N in exported diatom frustule (mmol/m^2)

$_{Sed}^{15}Fru$, ^{15}N in exported diatom frustule (mmol/m^2)

$_{Sed}^{14}Zoo$, ^{14}N in exported zooplankton (mmol/m^2)

$_{Sed}^{15}Zoo$, ^{15}N in exported zooplankton (mmol/m^2)

$^{14}ZooFood$, ^{14}N consumed by zooplankton (mmol/m^3/day)

$^{15}ZooFood$, ^{15}N consumed by zooplankton (mmol/m^3/day)

MLD_{summer}, Mixed Layer Depth (MLD) in summertime (m)

$M_{Tmin-Srf}$, mixing between the T$_{min}$ layer and the surface (m^3/day)

$M_{Tmin-CDW}$, mixing between the T$_{min}$ layer and CDW (m^3/day)

$M_{Upwelling}$, upwelling of CDW (m^3/day)

$Vmax_{NO3}$, Monod maximum NO_3^- assimilation rate (mmol/m³/day)

$K_{\frac{1}{2}NO3}$, Monod NO_3^- assimilation ½ saturation constant (mmol/m³)

$\kappa_{dtm-sink}$, Diatoms sinking from surface ocean (%/day)

$\kappa_{remineralization}$, Remineralization of sinking diatoms and zooplankton fecal pellets (%/day)

$\kappa_{zoo-dtm-feeding}$, Zooplankton consumption of diatoms (%/day)

$\kappa_{zoo-phyto-feeding}$, Zooplankton consumption of non-diatom phytoplankton (%/day)

$\kappa_{zoo-digestion}$, Zooplankton assimilation of diatom/non-diatom phytoplankton biomass (%/day)

$\kappa_{zoo-metabolism}$, Zooplankton release of NH_4^+ (%/day)

$\kappa_{Phyto-NH4-uptake}$, Non-diatom phytoplankton uptake of NH_4^+ (%/day)

$\kappa_{Phyto-NH4-release}$, Non-diatom phytoplankton release of NH_4^+ (%/day)

$\kappa_{NH4-nitrification}$, NH_4^+ nitrification (%/day)

$^{15}\alpha_{dtm-NO3}$, fractionation factor of diatom NO_3^- assimilation

$^{15}\alpha_{zoo-metabolism}$, fractionation factor of zooplankton metabolism

$^{15}\alpha_{zoo-digestion}$, fractionation factor of zooplankton digestion

$^{15}\alpha_{NH4-nitrification}$, fractionation factor of NH_4^+ nitrification

$^{15}\alpha_{remineralization}$, fractionation factor of remineralizing sinking organic matter

$^{15}\alpha_{FruBio}$, fractionation factor between diatom frustule and biomass

Equations
Equations S1 and S2 describe example ^{14}N and ^{15}N fluxes between reservoirs
Equations S3-S12 describe ^{14}N and ^{15}N partitioning between diatom biomass and frustule
Equations S13 and S14 describe ^{14}N and ^{15}N in diatom biomass sinking out of the surface ocean
Equations S15 and S16 describe ^{14}N and ^{15}N in diatom frustules sinking out of the surface ocean
Equations S17 and S18 describe ^{14}N and ^{15}N in diatom biomass in the surface ocean
Equations S19 and S20 describe ^{14}N and ^{15}N in diatom frustules in the surface ocean
Equations S21 and S22 describe ^{14}N and ^{15}N of material fed to zooplankton
Equations S23 and S24 describe ^{14}N and ^{15}N of zooplankton fecal pellets
Equations S25 and S26 describe ^{14}N and ^{15}N in zooplankton in the surface ocean
Equations S27 and S28 describe ^{14}N and ^{15}N in non-diatom phytoplankton in the surface ocean
Equations S29 and S30 describe ^{14}N and ^{15}N in diatom frustule export
Equations S31 and S32 describe ^{14}N and ^{15}N in diatom biomass export
Equations S33 and S34 describe ^{14}N and ^{15}N in zooplankton fecal pellet export
Equations S35 and S36 describe $^{14}NO_3^-$ and $^{15}NO_3^-$ in the surface ocean
Equations S37 and S38 describe $^{14}NH_4^+$ and $^{15}NH_4^+$ in the surface ocean
Equations S39 and S40 describe $^{14}NO_3^-$ and $^{15}NO_3^-$ in the temperature minimum layer
Equations S41 and S42 describe $^{14}NH_4^+$ and $^{15}NH_4^+$ in the temperature minimum layer

$$^{15}F\left[^{15}A, {}^{14}A, {}^{14}F, {}^{15}\alpha\right] = {}^{15}A * \left(1 - \left(\frac{^{14}A - {}^{14}F}{^{14}A}\right)^{^{15}\alpha}\right) \tag{eq. S1}$$

$$^{15}F\left[^{15}A, {}^{14}A, \kappa * {}^{14}A, {}^{15}\alpha\right] = {}^{15}A * \left(1 - (1 - \kappa)^{^{15}\alpha}\right) \tag{eq. S2}$$

$$R = \frac{(^{14}Fr + {}^{15}Fr)}{{}^{14}Fr + {}^{15}Fr + {}^{14}B + {}^{15}B} \tag{eq. S3}$$

$$\left(\frac{{}^{15}Fr}{{}^{14}Fr}\right) = {}^{15}\alpha_{FruBio}\left(\frac{{}^{15}B}{{}^{14}B}\right) \tag{eq. S4}$$

$$^{15}T = {}^{15}Fr + {}^{15}B \tag{eq. S5}$$

$$^{14}T = {}^{14}Fr + {}^{14}B \tag{eq. S6}$$

$$^{14}T = \left(\frac{Vmax_{NO3} * Srf^{14}_{NO3}}{Srf^{14}_{NO3} + K_{\frac{1}{2}NO3}}\right) \tag{eq. S7}$$

$$^{15}T = F[\left(\frac{Vmax_{NO3} * Srf^{14}_{NO3}}{Srf^{14}_{NO3} + K_{\frac{1}{2}NO3}}\right), {}^{15}\alpha_{dtm-NO3}] \tag{eq. S8}$$

$$^{14}Fr = R\left({}^{14}T + {}^{15}T\right) - {}^{15}Fr \tag{eq. S9}$$

$$^{14}B = {}^{14}T - {}^{14}Fr = {}^{14}T - \left(R\left({}^{14}T + {}^{15}T\right) - {}^{15}Fr\right) \tag{eq. S10}$$

$$^{15}B = {}^{15}T - {}^{15}Fr \tag{eq. S11}$$

$$\left(\frac{{}^{15}Fr}{R\left({}^{14}T + {}^{15}T\right) - {}^{15}Fr}\right) = {}^{15}\alpha_{FruBio}\left(\frac{{}^{15}T - {}^{15}Fr}{{}^{14}T - \left(R\left({}^{14}T + {}^{15}T\right) - {}^{15}Fr\right)}\right)$$

$$^{15}Fr * \left({}^{14}T - \left(R\left({}^{14}T + {}^{15}T\right) - {}^{15}Fr\right)\right) = {}^{15}\alpha_{FruBio}\left({}^{15}T - {}^{15}Fr\right) * \left(R\left({}^{14}T + T^{15}\right) - {}^{15}Fr\right)$$

$$\left({}^{15}Fr\right)^2 + {}^{15}Fr\left({}^{14}T - R\left({}^{14}T + {}^{15}T\right)\right)$$

$$= {}^{15}\alpha_{FruBio}\left({}^{15}Fr\right)^2 - {}^{15}Fr\left({}^{15}\alpha_{FruBio}R\left({}^{14}T + {}^{15}T\right) + {}^{15}\alpha_{FruBio}{}^{15}T\right)$$

$$+ {}^{15}\alpha_{FruBio}{}^{15}T\, R\left({}^{14}T + {}^{15}T\right)$$

$$\left({}^{15}Fr\right)^2\left(1 - {}^{15}\alpha_{FruBio}\right) + {}^{15}Fr\left({}^{14}T + \left({}^{15}\alpha_{FruBio} - 1\right)R\left({}^{14}T + {}^{15}T\right) + {}^{15}\alpha_{FruBio}{}^{15}T\right)$$

$$- {}^{15}\alpha_{FruBio}{}^{15}T\, R\left({}^{14}T + {}^{15}T\right) = 0$$

$$a = \left(1 - {}^{15}\alpha_{FruBio}\right)$$

$$b = \left({}^{14}T + \left({}^{15}\alpha_{FruBio} - 1\right)R\left({}^{14}T + {}^{15}T\right) + {}^{15}\alpha_{FruBio}{}^{15}T\right)$$

$$c = -^{15}\alpha_{FruBio} \, ^{15}T \, R\left(^{14}T + ^{15}T\right)$$

$$^{15}Fr = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \qquad \text{(eq. S12)}$$

$$_{Sink}^{14}Dtm = \kappa_{dtm-sink} * {}_{Srf}^{14}Dtm \qquad \text{(eq. S13)}$$

$$_{Sink}^{15}Dtm = \kappa_{dtm-sink} * {}_{Srf}^{15}Dtm \qquad \text{(eq. S14)}$$

$$_{Sink}^{14}Fru = (\kappa_{dtm-sink} + \kappa_{zoo-dtm-feeding}) * {}_{Srf}^{14}Fru \qquad \text{(eq. S15)}$$

$$_{Sink}^{15}Fru = (\kappa_{dtm-sink} + \kappa_{zoo-dtm-feeding}) * {}_{Srf}^{15}Fru \qquad \text{(eq. S16)}$$

$$\frac{d}{dt}\left({}_{Srf}^{14}Dtm\right) = {}^{14}B - {}_{Sink}^{14}Dtm - \kappa_{zoo-dtm-feeding} * {}_{Srf}^{14}Dtm \qquad \text{(eq. S17)}$$

$$\frac{d}{dt}\left({}_{Srf}^{15}Dtm\right) = {}^{15}B - {}_{Sink}^{15}Dtm - \kappa_{zoo-dtm-feeding} * {}_{Srf}^{15}Dtm \qquad \text{(eq. S18)}$$

$$\frac{d}{dt}\left({}_{Srf}^{14}Fru\right) = {}^{14}Fr - {}_{Sink}^{14}Fru \qquad \text{(eq. S19)}$$

$$\frac{d}{dt}\left({}_{Srf}^{15}Fru\right) = {}^{15}Fr - {}_{Sink}^{15}Fru \qquad \text{(eq. S20)}$$

$$^{14}ZooFood = \kappa_{zoo-phyto-feeding} * {}_{Srf}^{14}Phyto + \kappa_{zoo-dtm-feeding} * {}_{Srf}^{14}Dtm \qquad \text{(eq. S21)}$$

$$^{15}ZooFood = \kappa_{zoo-phyto-feeding} * {}_{Srf}^{15}Phyto + \kappa_{zoo-dtm-feeding} * {}_{Srf}^{15}Dtm \qquad \text{(eq. S22)}$$

$$^{14}FecalPellet = {}^{14}ZooFood - \kappa_{zoo-digestion} * {}^{14}ZooFood \qquad \text{(eq. S23)}$$

$$^{15}FecalPellet = {}^{15}ZooFood - F[\kappa_{zoo-digestion} * {}^{14}ZooFood, {}^{15}\alpha_{zoo-digestion}] \qquad \text{(eq. S24)}$$

$$\frac{d}{dt}\left({}_{Srf}^{14}Zoo\right) = \kappa_{Zoo-digestion} * {}^{14}ZooFood - \kappa_{zoo-metabolism} * {}_{Srf}^{14}Zoo \qquad \text{(eq. S25)}$$

$$\frac{d}{dt}\left({}_{Srf}^{15}Zoo\right) = F[\kappa_{zoo-digestion} * {}^{14}ZooFood, {}^{15}\alpha_{zoo-digestion}] - F[\kappa_{zoo-metabolism} *$$

$$_{Srf}^{14}Zoo, {}^{15}\alpha_{zoo-metabolism}] \qquad \text{(eq. S26)}$$

$$\frac{d}{dt}\left({}_{Srf}^{14}Phyto\right) = \kappa_{Phyto-NH4-uptake} * {}_{Srf}^{14}NH4 - \kappa_{Phyto-NH4-release} *$$

$$_{Srf}^{14}Phyto - \kappa_{zoo-phyto-feeding} * {}_{Srf}^{14}Phyto \qquad \text{(eq. S27)}$$

$$\frac{d}{dt}\left({}_{Srf}^{15}Phyto\right) = \kappa_{Phyto-NH4-uptake} * {}_{Srf}^{15}NH4 - \kappa_{Phyto-NH4-release} *$$

$${}_{Srf}^{15}Phyto - \kappa_{zoo-phyto-feeding} * {}_{Srf}^{15}Phyto \qquad \text{(eq. S28)}$$

$$\frac{d}{dt}\left({}_{Sed}^{14}Fru\right) = MLD_{summer} * {}_{Sink}^{14}Fru \qquad \text{(eq. S29)}$$

$$\frac{d}{dt}\left({}_{Sed}^{15}Fru\right) = MLD_{summer} * {}_{Sink}^{15}Fru \qquad \text{(eq. S30)}$$

$$\frac{d}{dt}\left({}_{Sed}^{14}Dtm\right) = MLD_{summer} * (1 - \kappa_{remineralization}) * {}_{Sink}^{14}Dtm \qquad \text{(eq. S31)}$$

$$\frac{d}{dt}\left({}_{Sed}^{15}Dtm\right) = MLD_{summer} * \left({}_{Sink}^{15}Dtm - F[\kappa_{remineralization} * {}_{Sink}^{14}Dtm, {}^{15}\alpha_{remineralization}]\right)$$

$$\text{(eq. S32)}$$

$$\frac{d}{dt}\left({}_{Sed}^{14}Zoo\right) = MLD_{summer} * (1 - \kappa_{remineralization}) * {}^{14}FecalPellet \qquad \text{(eq. S33)}$$

$$\frac{d}{dt}\left({}_{Sed}^{15}Zoo\right) = MLD_{summer} * ({}^{15}FecalPellet - F[\kappa_{remineralization} *$$

$${}^{14}FecalPellet, {}^{15}\alpha_{remineralization}]) \qquad \text{(eq. S34)}$$

$$\frac{d}{dt}\left({}_{Srf}^{14}NO3\right) = \frac{(M_{Tmin-Srf} + M_{Upwelling})}{V_{Srf}} * \left({}_{Tmin}^{14}NO3 - {}_{Srf}^{14}NO3\right) - \left(\frac{Vmax_{NO3} * {}_{Srf}^{14}NO3}{{}_{Srf}^{14}NO3 + K_{\frac{1}{2}NO3}}\right) +$$

$$\kappa_{NH4-nitrification} * {}_{Srf}^{14}NH4 \qquad \text{(eq. S35)}$$

$$\frac{d}{dt}\left({}_{Srf}^{15}NO3\right) = \frac{(M_{Tmin-Srf} + M_{Upwelling})}{V_{Srf}} * \left({}_{Tmin}^{15}NO3 - {}_{Srf}^{15}NO3\right) -$$

$$F[\left(\frac{Vmax_{NO3} * {}_{Srf}^{14}NO3}{{}_{Srf}^{14}NO3 + K_{\frac{1}{2}NO3}}\right), {}^{15}\alpha_{dtm-NO3}] + F[\kappa_{NH4-nitrification} * {}_{Srf}^{14}NH4, {}^{15}\alpha_{NH4-nitrification}]$$

$$\text{(eq. S36)}$$

$$\frac{d}{dt}\left({}_{Srf}^{14}NH4\right) = \frac{(M_{Tmin-Srf} + M_{Upwelling})}{V_{Srf}} * \left({}_{Tmin}^{14}NH4 - {}_{Srf}^{14}NH4\right) - (\kappa_{NH4-nitrification} *$$

$${}_{Srf}^{14}NH4) + (\kappa_{zoo-metabolism} * {}_{Srf}^{14}Zoo) - (\kappa_{Phyto-NH4-uptake} * {}_{Srf}^{14}NH4) +$$

$$(\kappa_{Phyto-NH4-release} * {}_{Srf}^{14}Phyto) \qquad \text{(eq. S37)}$$

$$\frac{d}{dt}\left({}_{Srf}^{15}NH4\right) = \frac{(M_{Tmin-Srf}+M_{Upwelling})}{V_{Srf}} * \left({}_{Tmin}^{15}NH4 - {}_{Srf}^{15}NH4\right) - F[\kappa_{NH4-nitrification} *$$

$${}_{Srf}^{14}NH4, {}^{15}\alpha_{NH4-nitrification}] + F[\kappa_{zoo-metabolism} * {}_{Srf}^{14}Zoo, {}^{15}\alpha_{zoo-metabolism}] -$$

$$(\kappa_{Phyto-NH4-uptake} * {}_{Srf}^{15}NH4) + (\kappa_{Phyto-NH4-release} * {}_{Srf}^{15}Phyto) \qquad \text{(eq. S38)}$$

$$\frac{d}{dt}\left({}_{Tmin}^{14}NO3\right) = \frac{(M_{Tmin-Srf})}{V_{Tmin}} * \left({}_{Surf}^{14}NO3\right) + \frac{(M_{Tmin-CDW} + M_{Upwelling})}{V_{Tmin}} * \left({}_{CDW}^{14}NO3\right) -$$

$$\frac{(M_{Tmin-Srf}+M_{Upwelling}+M_{Tmin-CDW})}{V_{Tmin}} * \left({}_{Tmin}^{14}NO3\right) + (\kappa_{NH4-nitrification} * {}_{Tmin}^{14}NH4) \qquad \text{(eq. S39)}$$

$$\frac{d}{dt}\left({}_{Tmin}^{15}NO3\right) = \frac{(M_{Tmin-Srf})}{V_{Tmin}} * \left({}_{Surf}^{15}NO3\right) + \frac{(M_{Tmin-CDW} + M_{Upwelling})}{V_{Tmin}} * \left({}_{CDW}^{15}NO3\right) -$$

$$\frac{(M_{Tmin-Srf}+M_{Upwelling}+M_{Tmin-CDW})}{V_{Tmin}} * \left({}_{Tmin}^{15}NO3\right) + F[\kappa_{NH4-nitrification} *$$

$${}_{Tmin}^{14}NH4, {}^{15}\alpha_{NH4-nitrification}] \qquad \text{(eq. S40)}$$

$$\frac{d}{dt}\left({}_{Tmin}^{14}NH4\right) = \frac{(M_{Tmin-Srf})}{V_{Tmin}} * \left({}_{Srf}^{14}NH4\right) - \frac{(M_{Tmin-Srf}+M_{Upwelling}+M_{Tmin-CDW})}{V_{Tmin}} * \left({}_{Tmin}^{14}NH4\right) -$$

$$(\kappa_{NH4-nitrification} * {}_{Tmin}^{14}NH4) + (\frac{V_{Srf}}{V_{Tmin}} * \kappa_{remineralization} * {}_{Sink}^{14}Dtm)+(\frac{V_{Srf}}{V_{Tmin}} *$$

$$\kappa_{remineralization} * {}^{14}FecalPellet) \qquad \text{(eq. S41)}$$

$$\frac{d}{dt}\left({}_{Tmin}^{15}NH4\right) = \frac{(M_{Tmin-Srf})}{V_{Tmin}} * \left({}_{Srf}^{15}NH4\right) - \frac{(M_{Tmin-Srf}+M_{Upwelling}+M_{Tmin-CDW})}{V_{Tmin}} * \left({}_{Tmin}^{15}NH4\right) -$$

$$F[\kappa_{NH4-nitrification} * {}_{Tmin}^{14}NH4, {}^{15}\alpha_{NH4-nitrification}]+(\frac{V_{Srf}}{V_{Tmin}} * F[\kappa_{remineralization} *$$

$${}_{Sink}^{14}Dtm, {}^{15}\alpha_{remineralization}])+(\frac{V_{Srf}}{V_{Tmin}} * F[\kappa_{remineralization} *$$

$${}^{14}FecalPellet, {}^{15}\alpha_{remineralization}]) \qquad \text{(eq. S42)}$$

Supplement S2: Midglacial and glacial model results

Figures S1 and S2 show model results for the midglacial and glacial scenarios, analogous to the results presented in Figure 3 of the main text for the interglacial case.
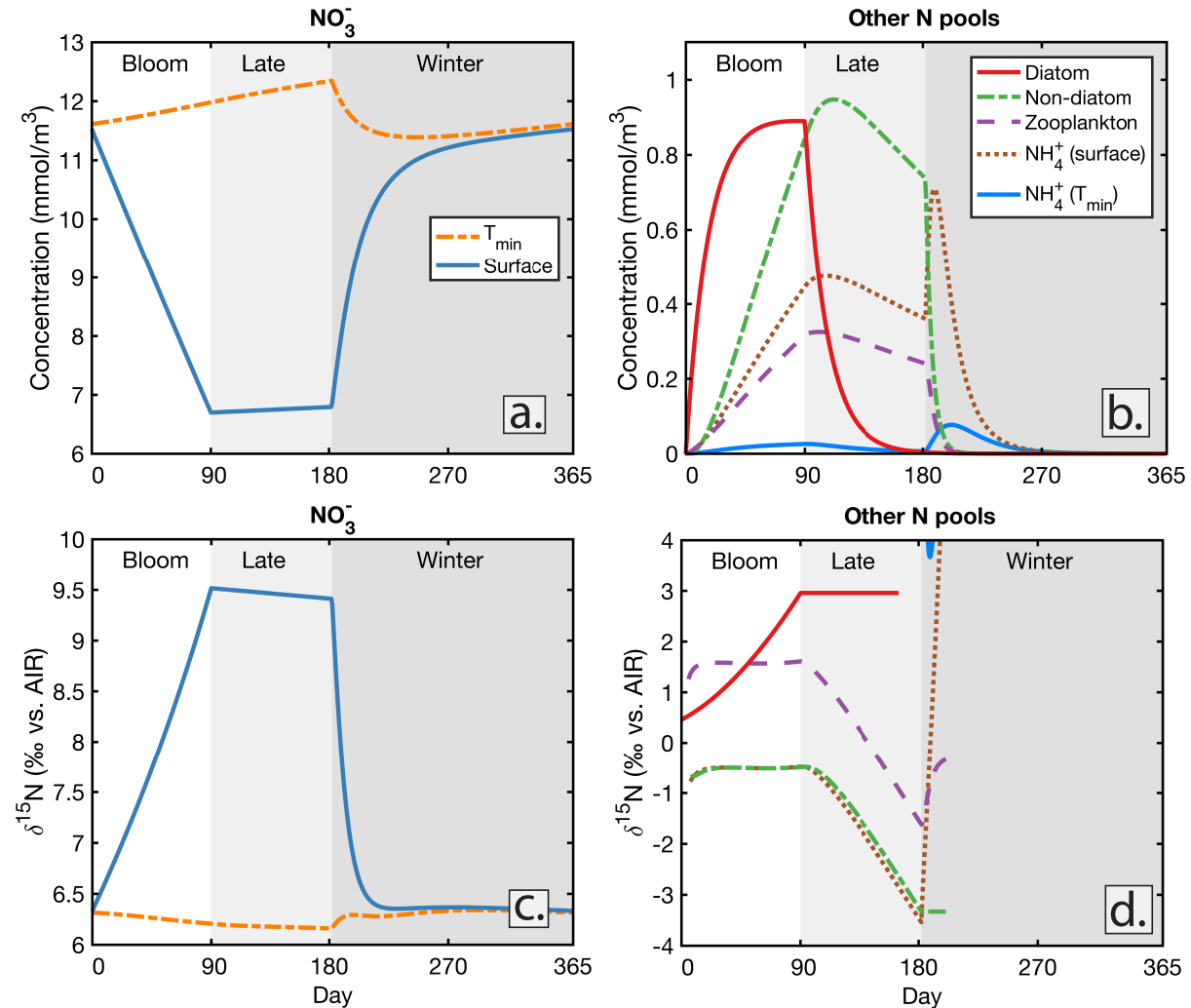

Figure S1: Steady-state model results for the midglacial scenario using the model reported in the main text. $\delta^{15}N$ values are plotted for all pools with N content > 0.01 mmol/m^3.
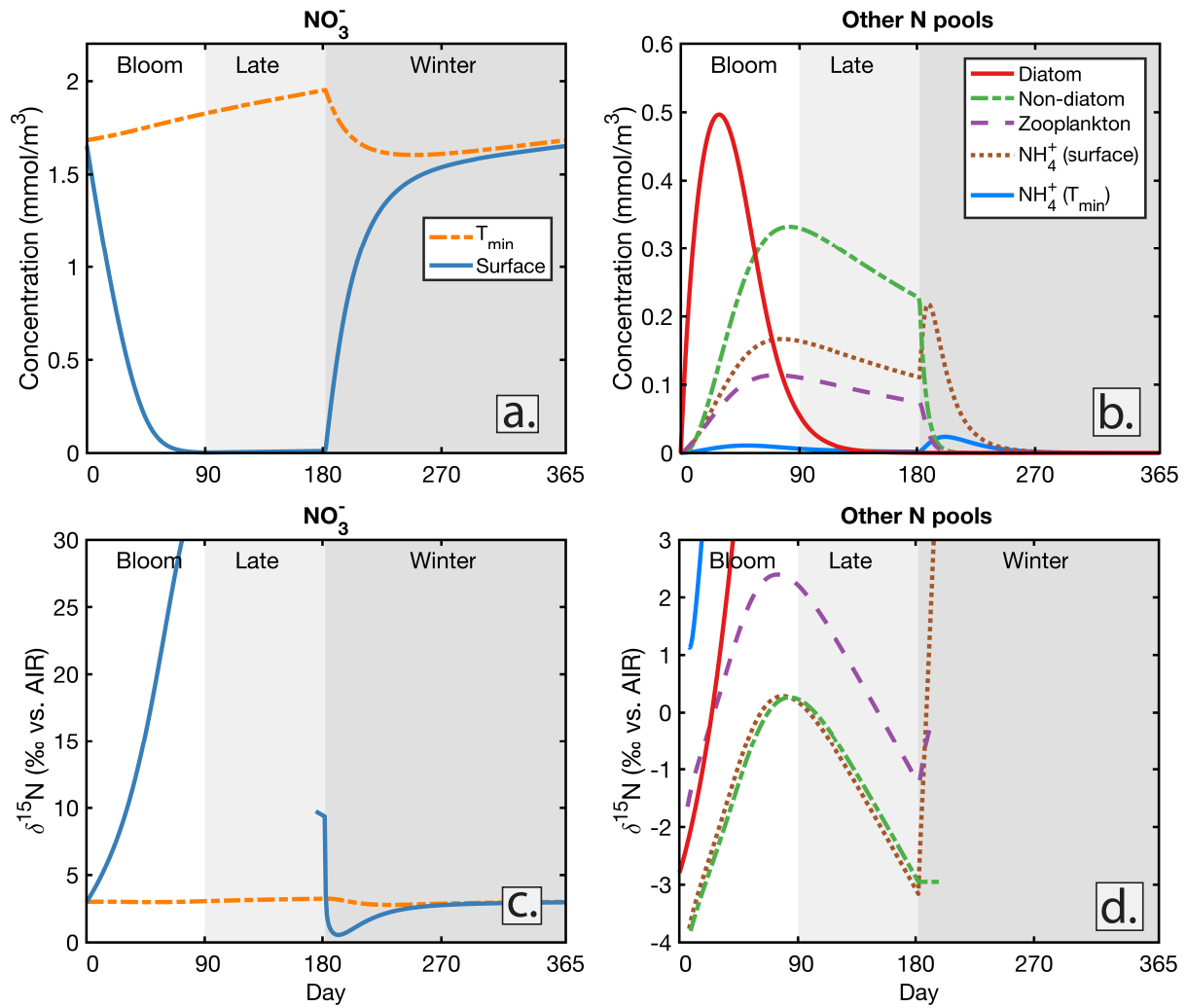
Figure S2: Steady-state model results for the glacial scenario using the model reported in the main text. δ¹⁵N values are plotted for all pools with N content > 0.01 mmol/m³.

Supplement S3: Model sensitivity to changing supply pathways

The model results reported in the main text are parametrized with 10 Sv of upwelling and 10 Sv of basal mixing across the base of the T_{min} layer / wintertime mixed layer. The 10 Sv of upwelling reflect the balance between total wind-driven Ekman pumping and a countervailing eddy transport (Marshall & Speer, 2012). However, the buoyancy dynamics at the surface of the Southern Ocean remain an area of active research, and there is uncertainty in the magnitude of upwelling water. Here we present model results for a range of values for the magnitudes of upwelling and basal mixing (Figures S3-S6). We then directly compare the results of supply exclusively from upwelling or basal mixing against the case of 10 Sv of each (Figures S7, S8, and S9). In Figure S3-S9 the choice of model parameters is the same as in the main text, which were calibrated to modern observations for the use of 10 Sv upwelling and 10 Sv of basal mixing.

When the model is run with 20 Sv of upwelling and no basal mixing, the movement of water from the summertime T_{min} layer into the surface ocean is doubled and end-summer $[NO_3^-]$ and NO_3^- $\delta^{15}N$ are drawn towards the values of CDW. Under this alternative circulation, end-summer $[NO_3^-]$ is elevated and end-summer NO_3^- $\delta^{15}N$ is reduced in both the surface and T_{min} layers. As a consequence, the $\delta^{15}N$ of exported diatoms is also reduced, and a larger reduction in gross NO_3^- supply is required to generate the elevated $\delta^{15}N_{db}$ measured in sediment cores (Studer et al., 2015). When the model is run with only basal mixing and no upwelling, end-summer $[NO_3^-]$ is reduced and end-summer NO_3^- $\delta^{15}N$ is elevated in both the surface and T_{min} layers relative to the case with mixed supply mechanisms. However, the change in gross water exchange required to achieve the observed rise in $\delta^{15}N_{db}$ is comparable among all three cases (within a few %), and thus our primary conclusion is unchanged regarding the large proportional reduction in surface-to-deep exchange required by paleoceanographic observations.

A potential gap in our simulations is that they fail to account for possible changes in the $[NO_3^-]$ or NO_3^- $\delta^{15}N$ of the boundary condition, such as might occur if CDW $[NO_3^-]$ changed during LGM or if the ice age AZ sampled a greater fraction of low-$[NO_3^-]$ water masses. Because the boundary condition is kept constant, the model only reaches elevated values of $\delta^{15}N_{db}$ by reducing the rate of water supply into the upper ocean (Figure 6). Conversely, a reduction in boundary $[NO_3^-]$ could also reduce the supply of N into the AZ surface and decrease the required decline in gross NO_3^- supply to attain the observed increase in $\delta^{15}N_{db}$. To address this argument, we present model results analogous to Figure 6b when $[NO_3^-]$ in CDW is reduced from 33.5 mmol/m^3 to 27 mmol/m^3 or 20 mmol/m^3 (Figure S10). In model results with an active N cycle where the residual circulation and basal mixing are reduced from 10 Sv to 0 Sv and CDW $[NO_3^-]$ is set at either 27.0 mmol/m^3 or 20.0 mmol/m^3 the model still requires >75% or >65% reduction in the gross supply of nutrients from depth. In the case without an active N cycle, the required decline in gross NO_3^- supply is reduced to be >50% or >30% when CDW $[NO_3^-]$ is 27.0 mmol/m^3 or 20.0 mmol/m^3, respectively. However, such $[NO_3^-]$ reductions are unlikely in CDW, which typifies much of the ocean's deep water today. CDW would have to undergo major changes in its origin and evolution to become so distinct in $[NO_3^-]$ from the rest of the deep ocean.
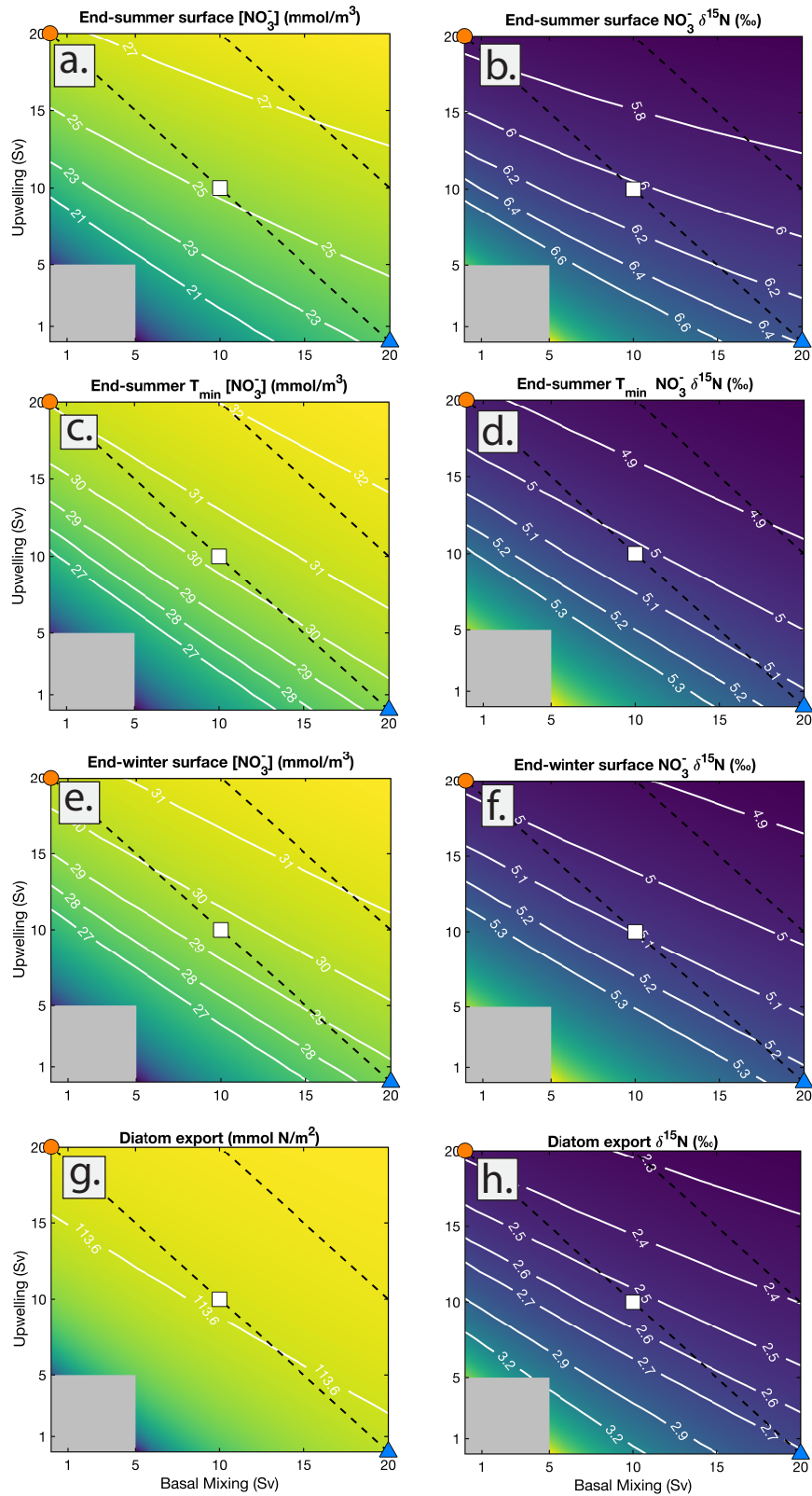
Figure S3: Model results with an active N cycle for moderate magnitudes of upwelling and basal mixing. White squares indicate scenarios discussed in the main text, blue upward triangles and orange circles indicate scenarios plotted in Figure S7.
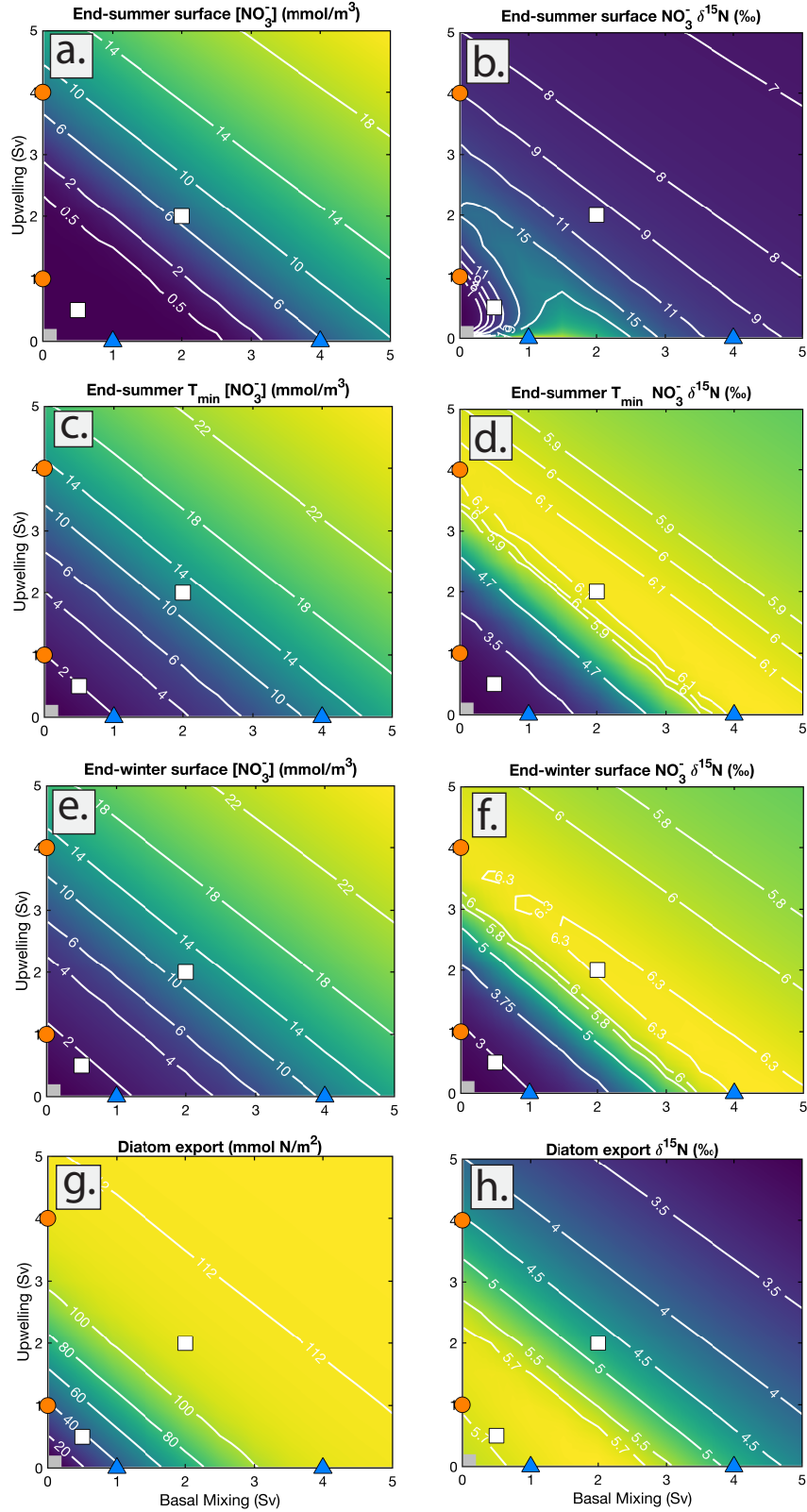
Figure S4: Model results with an active N cycle for low magnitudes of upwelling and basal mixing. White squares indicate scenarios discussed in the main text, blue upward triangles and orange circles indicate scenarios plotted in Figure S7.