Periodic Table of the Elements

What is the largest reservoir of nitrogen on the planet?

Main groups | Transition metals | Main groups

1 1A	2 2A	3 3B	4 4B	5 5B	6 6B	7 7B	8 8B	9 8B	10 8B	11 1B	12 2B	13 3A	14 4A	15 5A	16 6A	17 7A	18 8A
1 H 1.00794																	2 He 4.00260
3 Li 6.941	4 Be 9.01218											5 B 10.81	6 C 12.011	7 N 14.0067	8 O 15.9994	9 F 18.998403	10 Ne 20.1797
11 Na 22.98977	12 Mg 24.305											13 Al 26.98154	14 Si 28.0855	15 P 30.97376	16 S 32.066	17 Cl 35.453	18 Ar 39.948
19 K 39.0983	20 Ca 40.078	21 Sc 44.9559	22 Ti 47.88	23 V 50.9415	24 Cr 51.996	25 Mn 54.9380	26 Fe 55.847	27 Co 58.9332	28 Ni 58.69	29 Cu 63.546	30 Zn 65.39	31 Ga 69.72	32 Ge 72.61	33 As 74.9216	34 Se 78.96	35 Br 79.904	36 Kr 83.80
37 Rb 85.4678	38 Sr 87.62	39 Y 88.9059	40 Zr 91.224	41 Nb 92.9064	42 Mo 95.94	43 Tc (98)	44 Ru 101.07	45 Rh 102.9055	46 Pd 106.42	47 Ag 107.8682	48 Cd 112.41	49 In 114.82	50 Sn 118.710	51 Sb 121.757	52 Te 127.60	53 I 126.9045	54 Xe 131.29
55 Cs 132.9054	56 Ba 137.33	57 *La 138.9055	72 Hf 178.49	73 Ta 180.9479	74 W 183.85	75 Re 186.207	76 Os 190.2	77 Ir 192.22	78 Pt 195.08	79 Au 196.9665	80 Hg 200.59	81 Tl 204.383	82 Pb 207.2	83 Bi 208.9804	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra 226.0254	89 †Ac 227.0278	104 Rf (261)	105 Db (262)	106 Sg (266)	107 Bh (264)	108 Hs (269)	109 Mt (268)	110 (271)	111 (272)	112 (277)		114 (289)		116 (289)		118 (293)

*Lanthanide series	58 Ce 140.12	59 Pr 140.9077	60 Nd 144.24	61 Pm (145)	62 Sm 150.36	63 Eu 151.96	64 Gd 157.25	65 Tb 158.9254	66 Dy 162.50	67 Ho 164.9304	68 Er 167.26	69 Tm 168.9342	70 Yb 173.04	71 Lu 174.967
†Actinide series	90 Th 232.0381	91 Pa 231.0359	92 U 238.0289	93 Np 237.048	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (262)


What are some other forms of inorganic nitrogen?

Nitrogen: The Basics

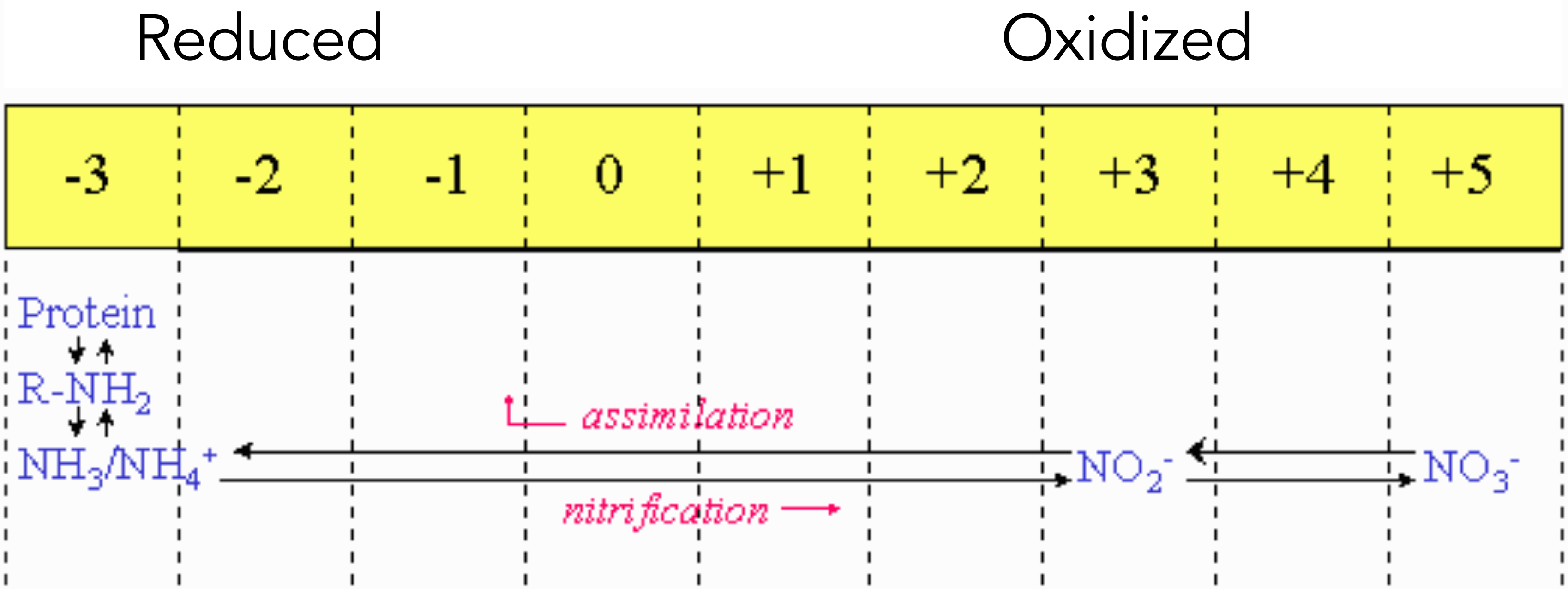
Nitrogen is (almost always) a limiting nutrient.

All plants (marine, aquatic, and terrestrial), phytoplankton, and bacteria can use NH_4 (ammonium) as a nitrogen source.

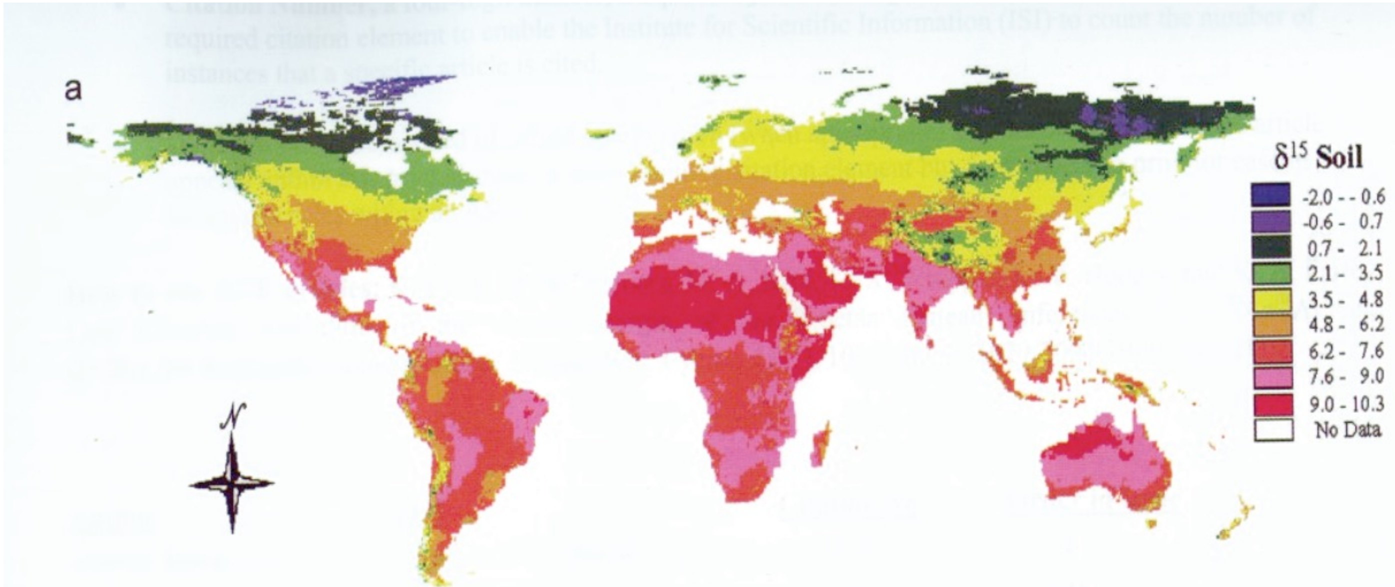
Most plants and some bacteria can use NO_3 (nitrate) as a nitrogen source.

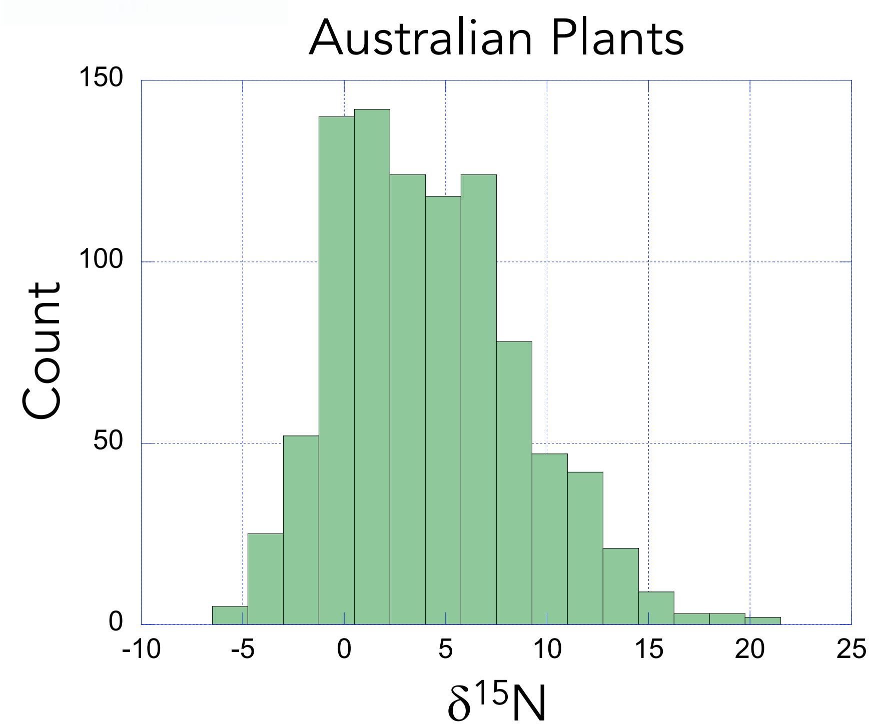
Only a few cyanobacteria and microbes can use N_2 as a nitrogen source.

Redox is Important: Controls Speciation in Compounds



What Controls $\delta^{15}N$ Variation in Soils and Plants?





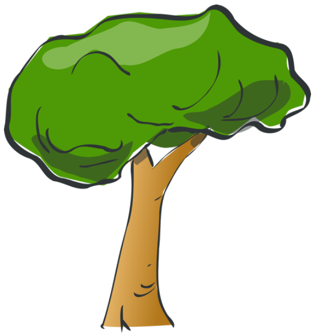
Major Themes

Chemical transformations are key to isotopic fractionation.

Although there are exceptions, the conversion of organic to inorganic material is most often the primary interest.

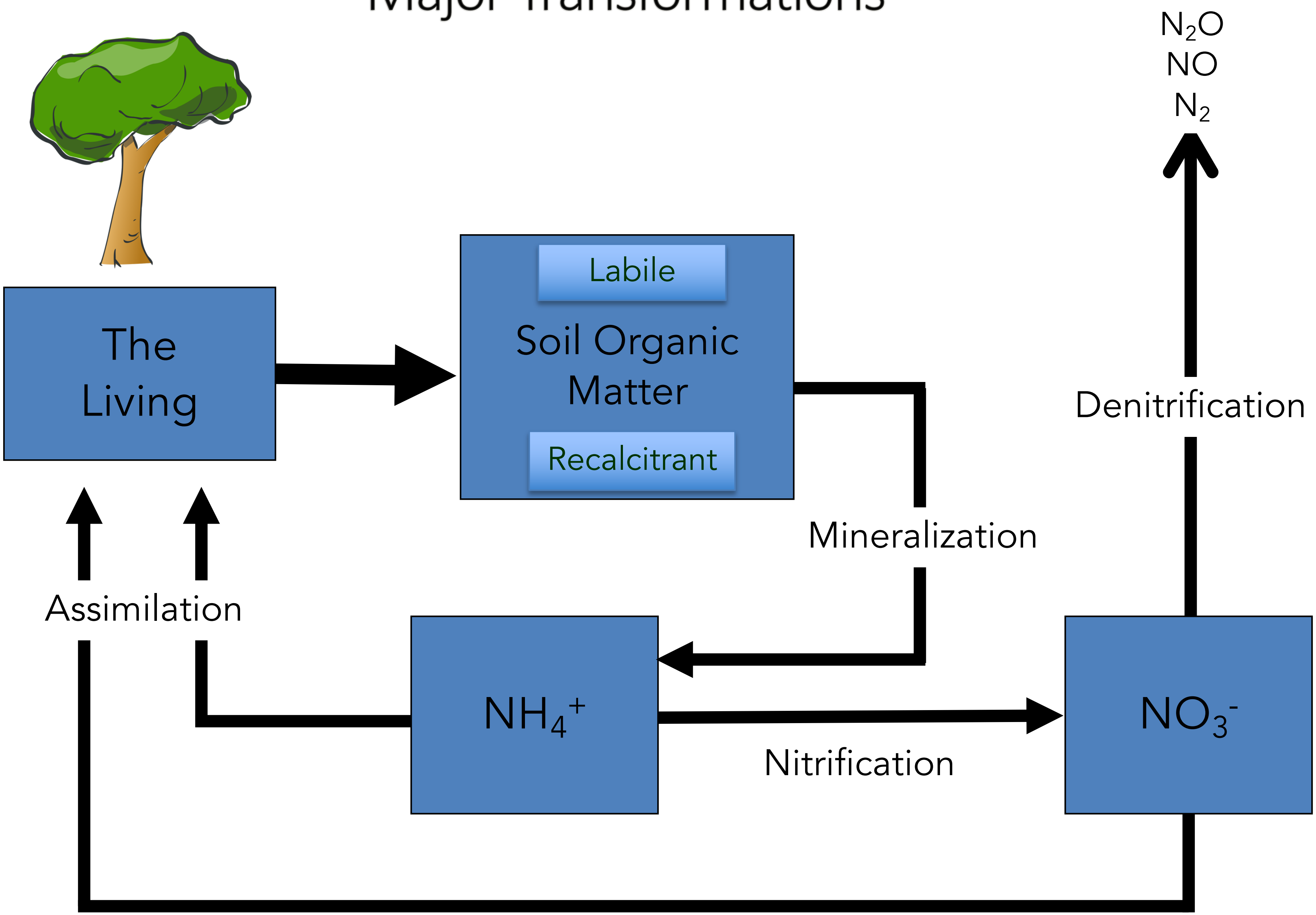
Separate internal cycling from additions and losses.

Chalkboard



The
Living

Major Transformations



Soil Processes: Observed $\Delta^{15}N$

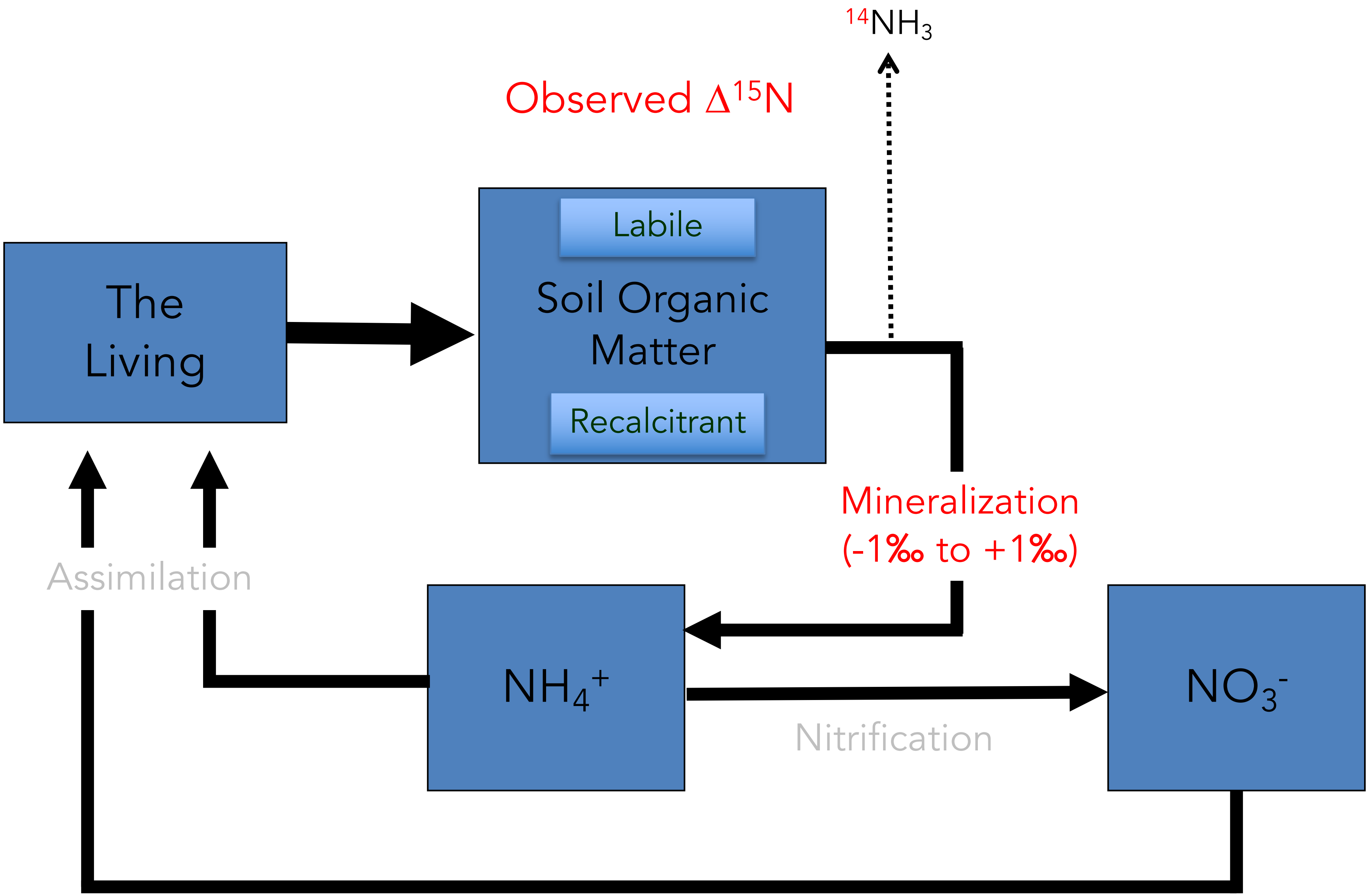
	Process	Fractionation (‰)	Source
Small	N_2 fixation	−2 to 2	(1)
	Assimilation	−1 to 1.6	(2)
Large	Nitrification	12 to 35	(3), (1)
	Denitrification	0 to 33, 26	(1), (4)
	Ammonia volatilization	20 to 27	(1)
Small	Mineralization	−1 to 1	(2)
	Ion exchange	−1 to −8	(5)
	Enzymatic hydrolysis	10 to 24	(6)
	N transfer, ECM fungi to plant host	8 to 10	(6)
	N transfer, AM fungi to plant host	0 to 3.5[a]	(7)

Positive values indicate that the reactant is enriched in ^{15}N (e.g., NH_4^+ in nitrification) and the product is depleted in ^{15}N (e.g., NO_3^- in nitrification). Sources: (1) Högberg (1997), (2) Kendall (1998), (3) Shearer and Kohl (1986), (4) Pörtl et al. (2007), (5) Hübner (1986), (6) Hobbie and Colpaert (2003), (7) Handley et al. (1999b)

ECM ectomycorrhizal, *AM* arbuscular mycorrhizal

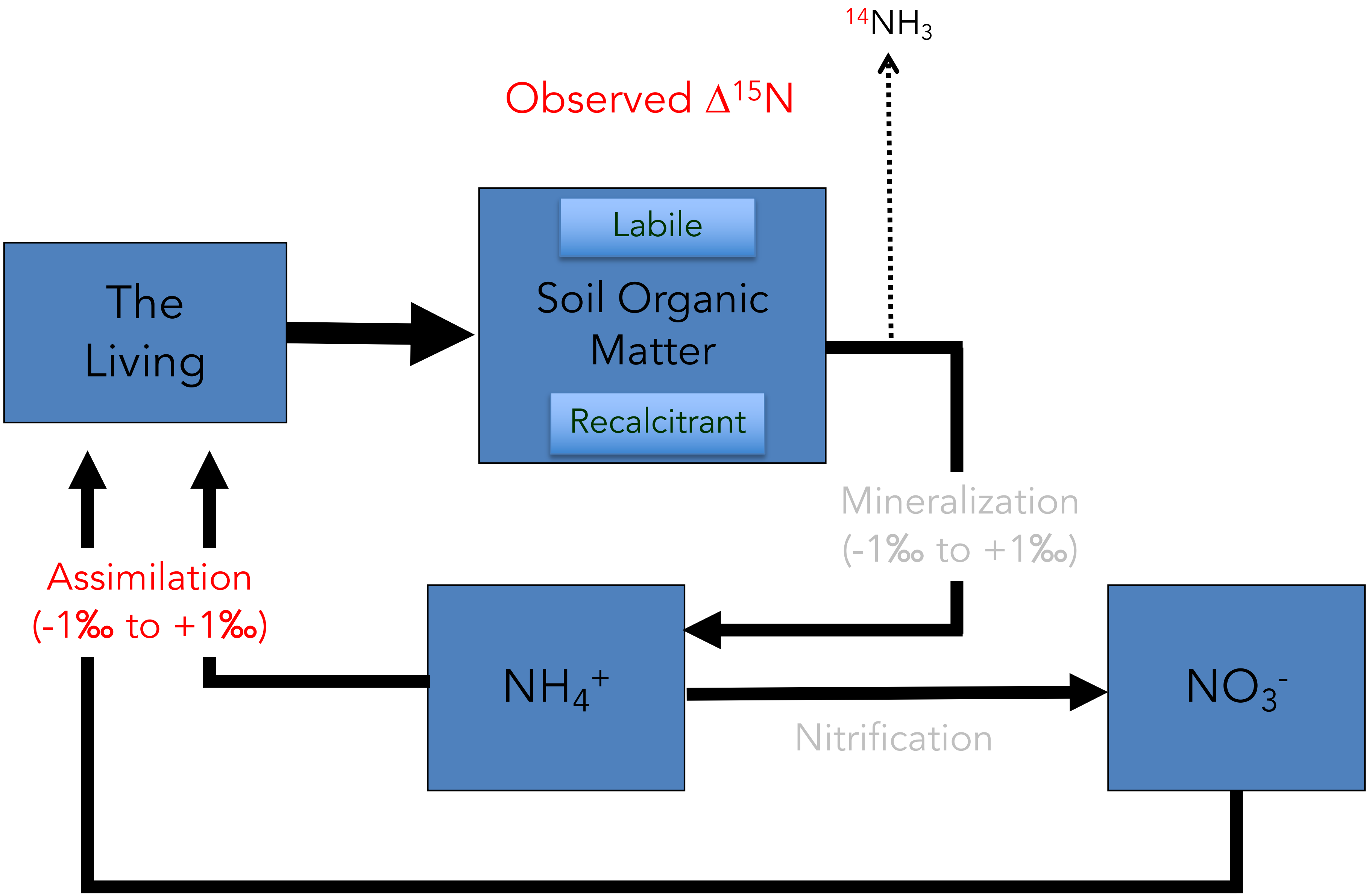
"Lighter Goes Faster"

Major Transformations



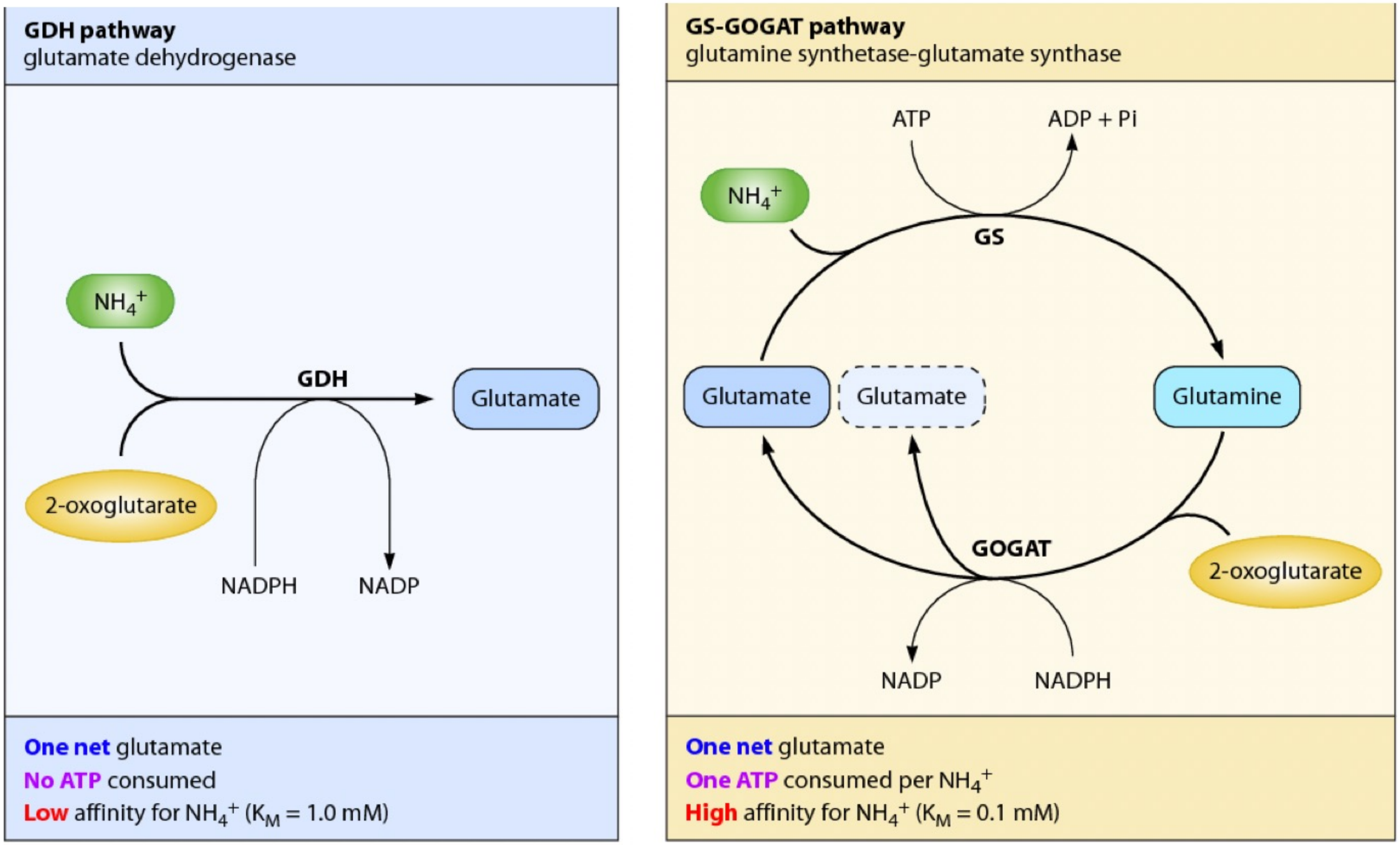
Positive values indicate reactant is enriched in ^{15}N, and the product is depleted in ^{15}N

Major Transformations



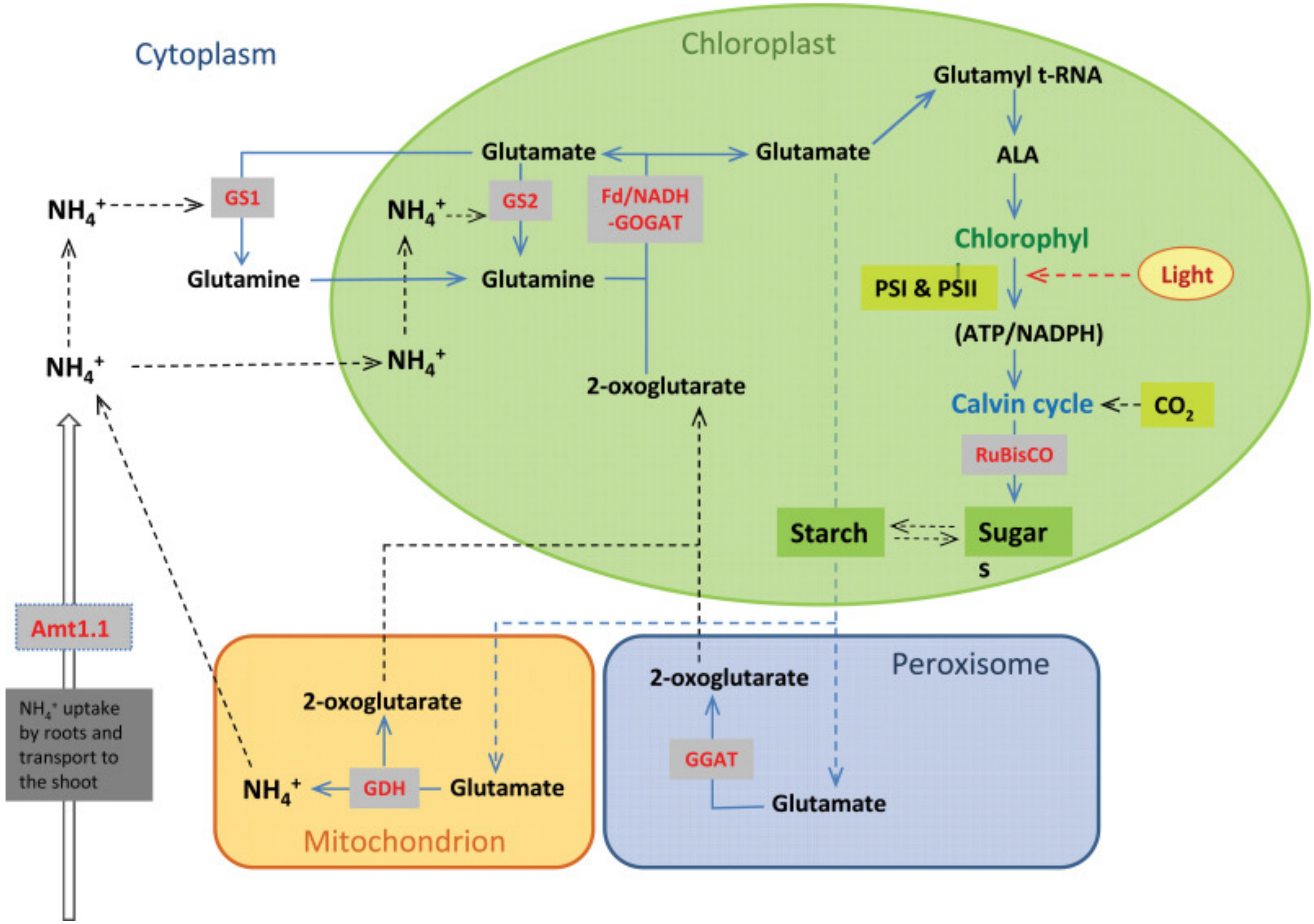
Positive values indicate reactant is enriched in ^{15}N, and the product is depleted in ^{15}N

Enzymes Associated with NH_4 Uptake



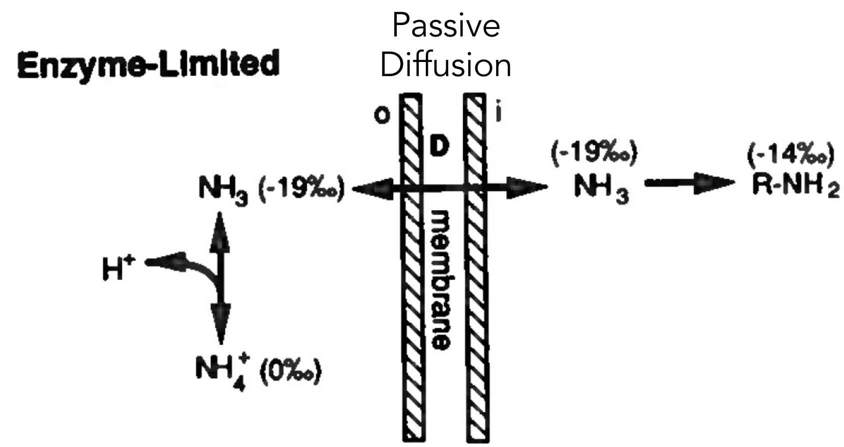
Van Heeswijk et al. 2013

Where Does This Occur?



Ranathunge et al. 2014

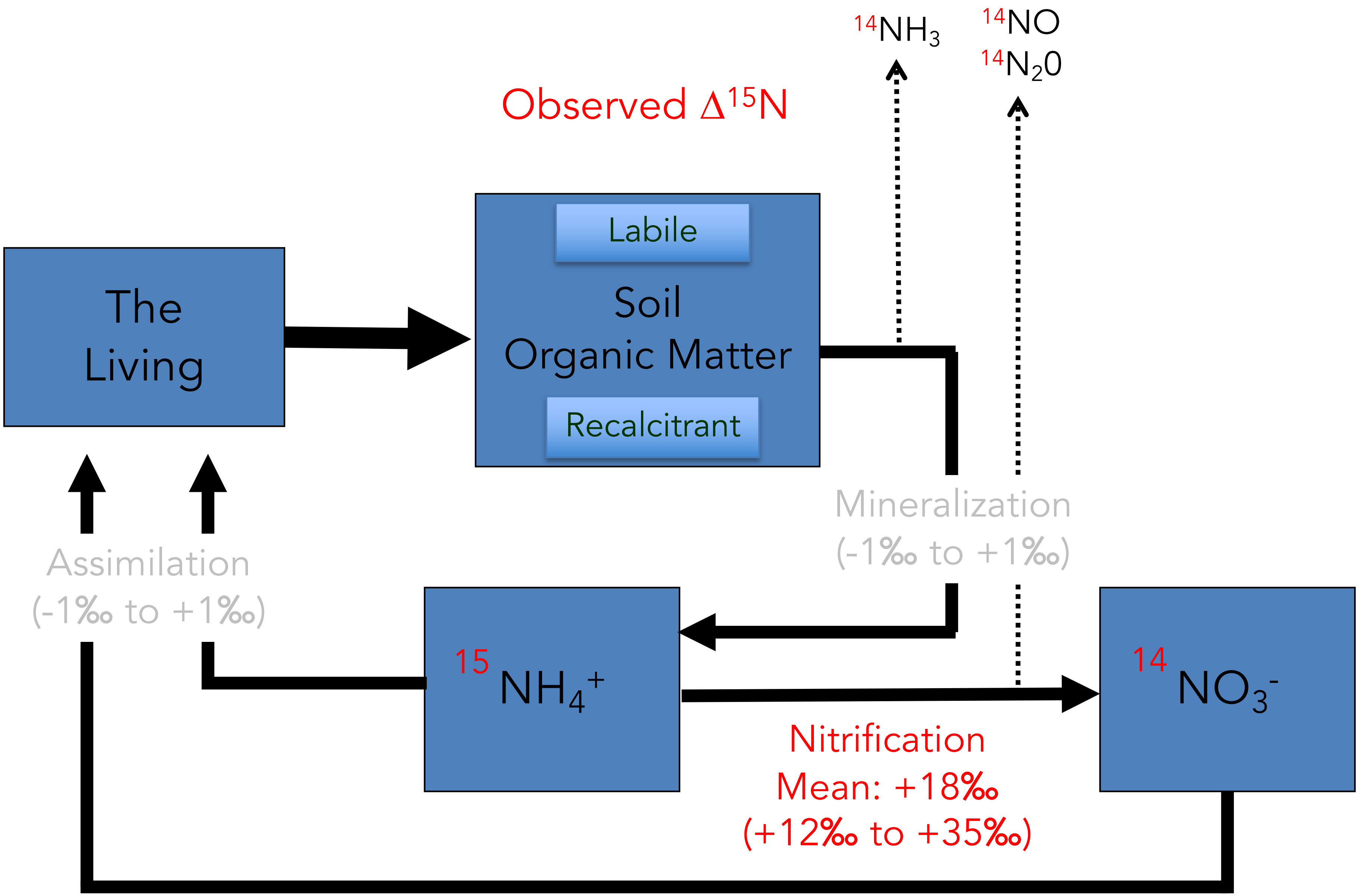
Fractionation During NH_4 Uptake



Intermediate $\Delta^{15}N$
(only equilibrium effect)
$NH_4 \longleftrightarrow NH_3 + H^+$

Fogel and Cifuentes 1993

Major Transformations



Positive values indicate reactant is enriched in ^{15}N, and the product is depleted in ^{15}N

Nitrification

$$2NH_4 + 3O_2 \longrightarrow 2NO_2 + 4H + 2H_2O$$

(*Nitrosomonas, Comammox*)

$$2NO_2 + O_2 \longrightarrow 2NO_3$$

(*Nitrobacter, Nitrospira, Comammox*)

OR

$$NH_3 + O_2 \longrightarrow NO_2 + 3H^+ + 2e^-$$

$$NO_2 + H_2O \longrightarrow NO_3 + 2H^+ + 2e^-$$

Nitrifying ammonia-oxidizing bacteria (AOB) and archaea (AOA)

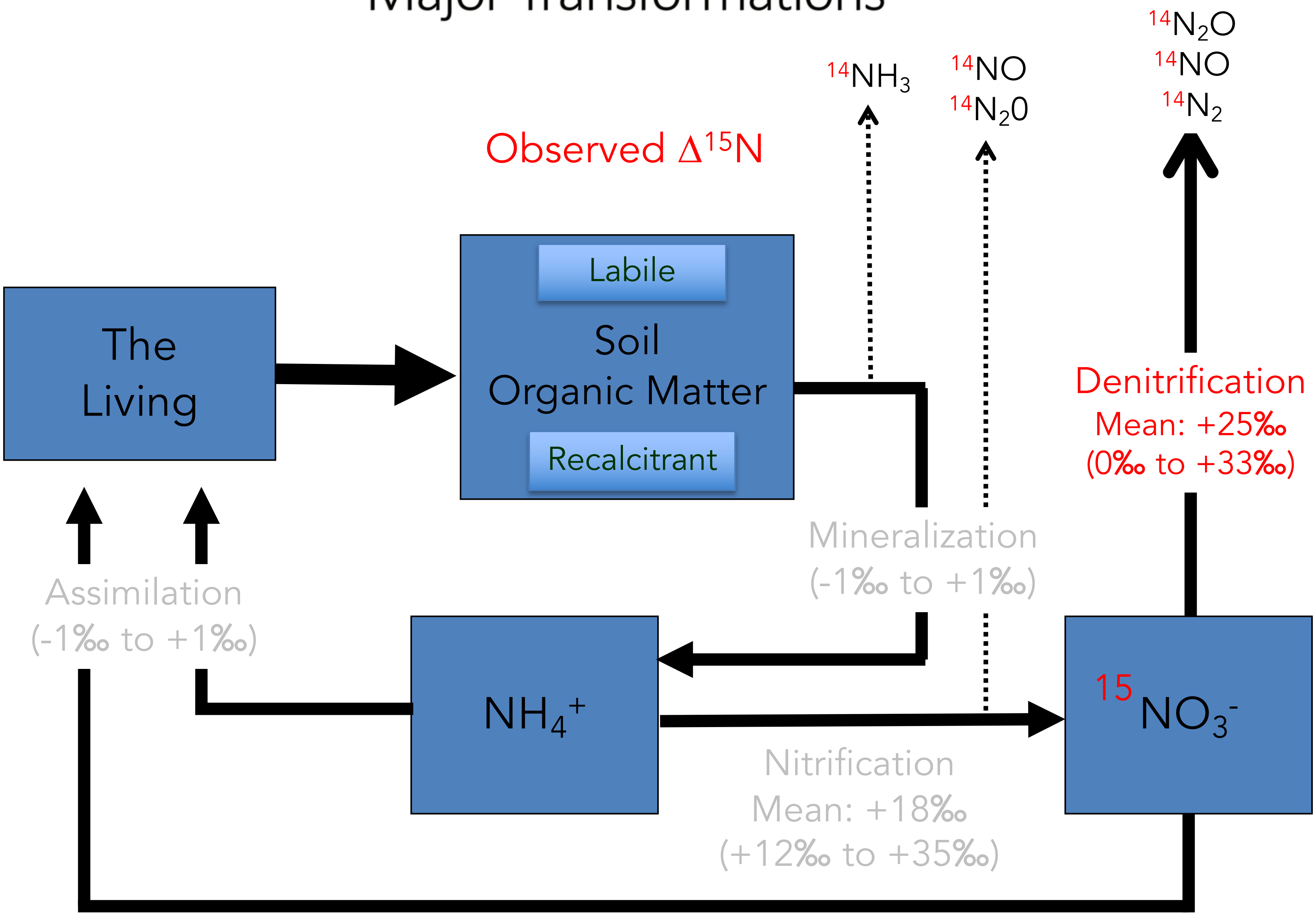
Nitrifying organisms are chemoautotrophs (use CO_2)

Nitrification takes place only in the presence of oxygen (aerobic)

Important in agricultural systems (converts NH_3 to NO_3)

Increases soil leaching because NO_3 is more soluble in water

Major Transformations



Positive values indicate reactant is enriched in ^{15}N, and the product is depleted in ^{15}N

Denitrification

$$NO_3 + 12H^+ + 10e^- = N_2 + 6H_2O$$

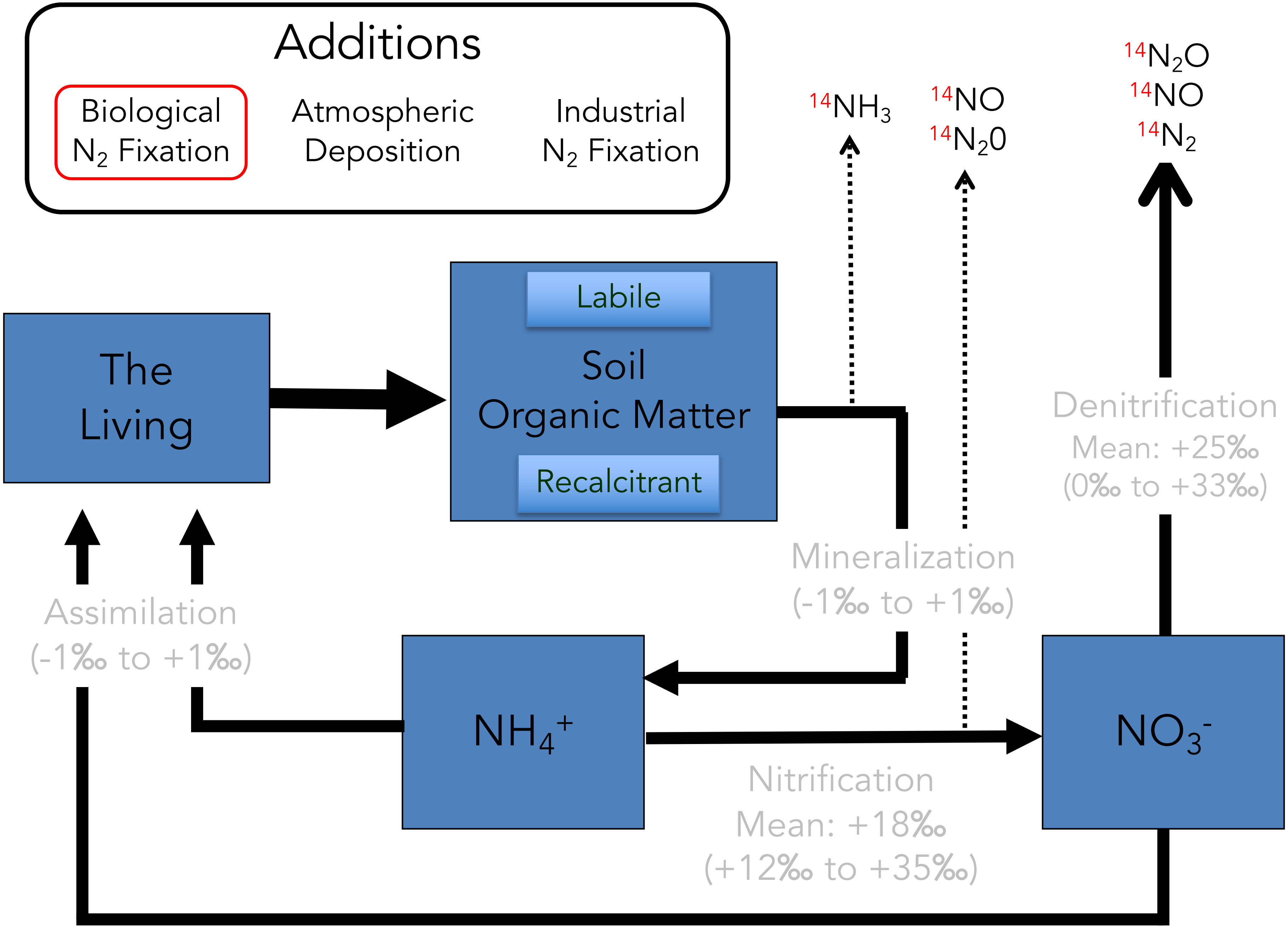
$$NO_3 \longrightarrow NO_2 \longrightarrow NO + N_2O \longrightarrow N_2$$

Denitrifying bacteria (nitrate reductase enzyme).

Takes place only in the *absence* of oxygen (anaerobic).

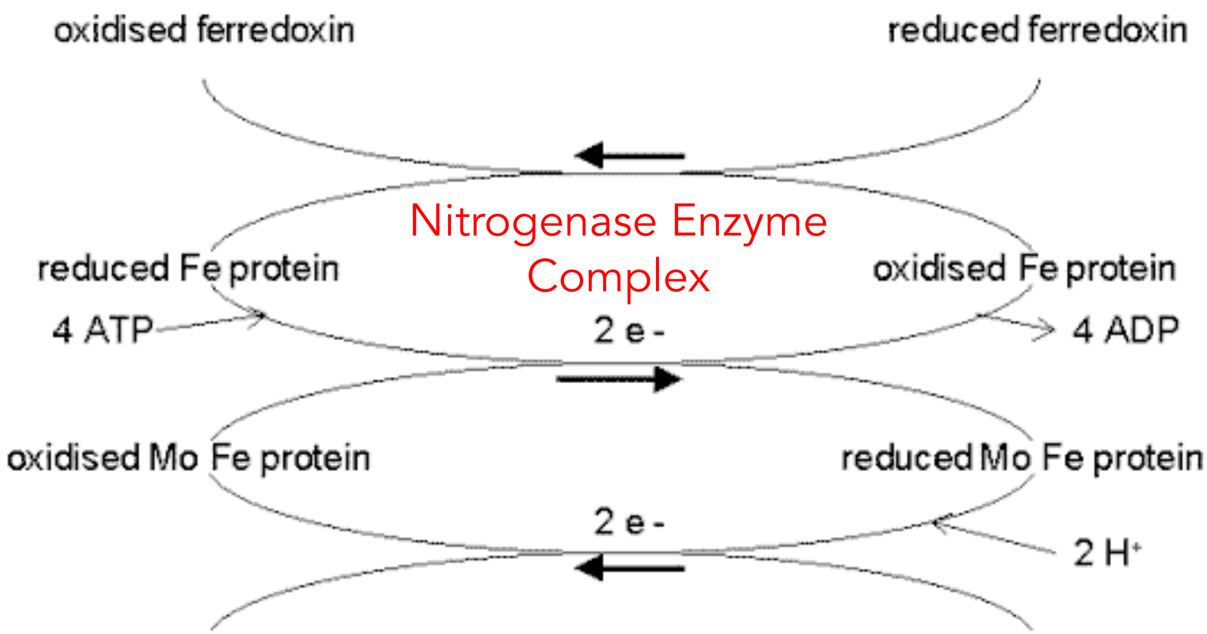
Deep soils, stagnant waters, ocean depths.

Lowers soil fertility by converting useful NO_3 into useless N_2.


Additions
Biological
N2 Fixation
Atmospheric
Deposition
Industrial
N2 Fixation
14NH3
14NO
14N20
14N2O
14NO
14N2
The
Living
Labile
Soil
Organic Matter
Recalcitrant
Denitrification
Mean: +25‰
(0‰ to +33‰)
Mineralization
(-1‰ to +1‰)
Assimilation
(-1‰ to +1‰)
NH4+
NO3-
Nitrification
Mean: +18‰
(+12‰ to +35‰)

Nitrogen Fixation: Nitrogenase

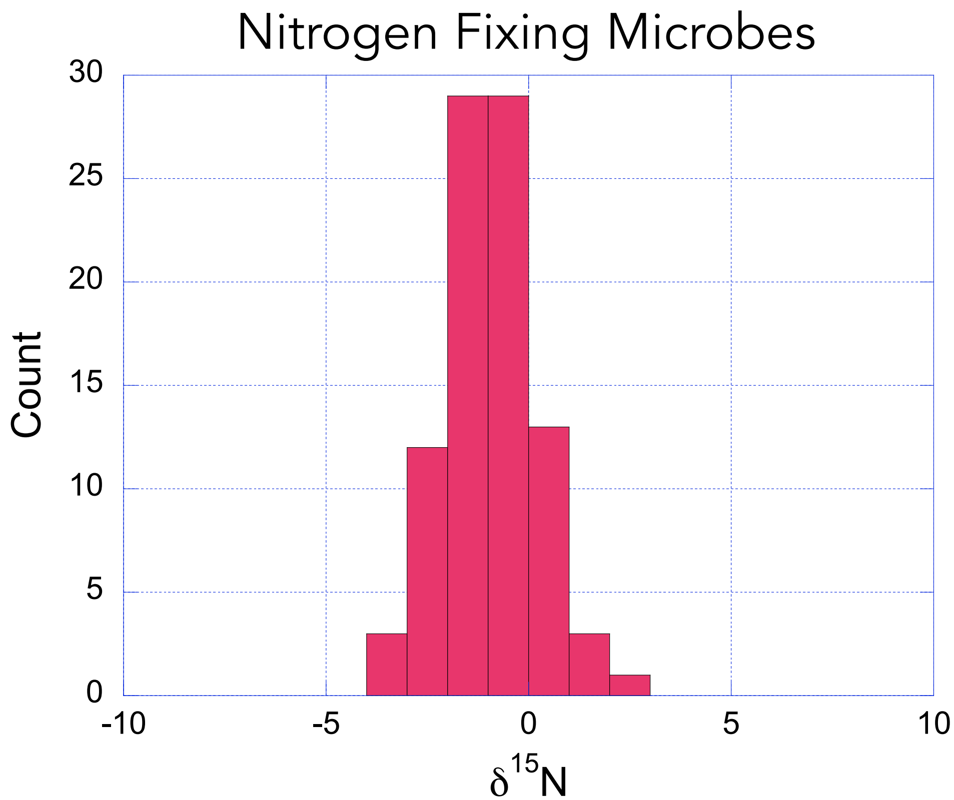
Fe Protein and Mo-Fe Protein
Reduced Ferrodoxin (electron supply)

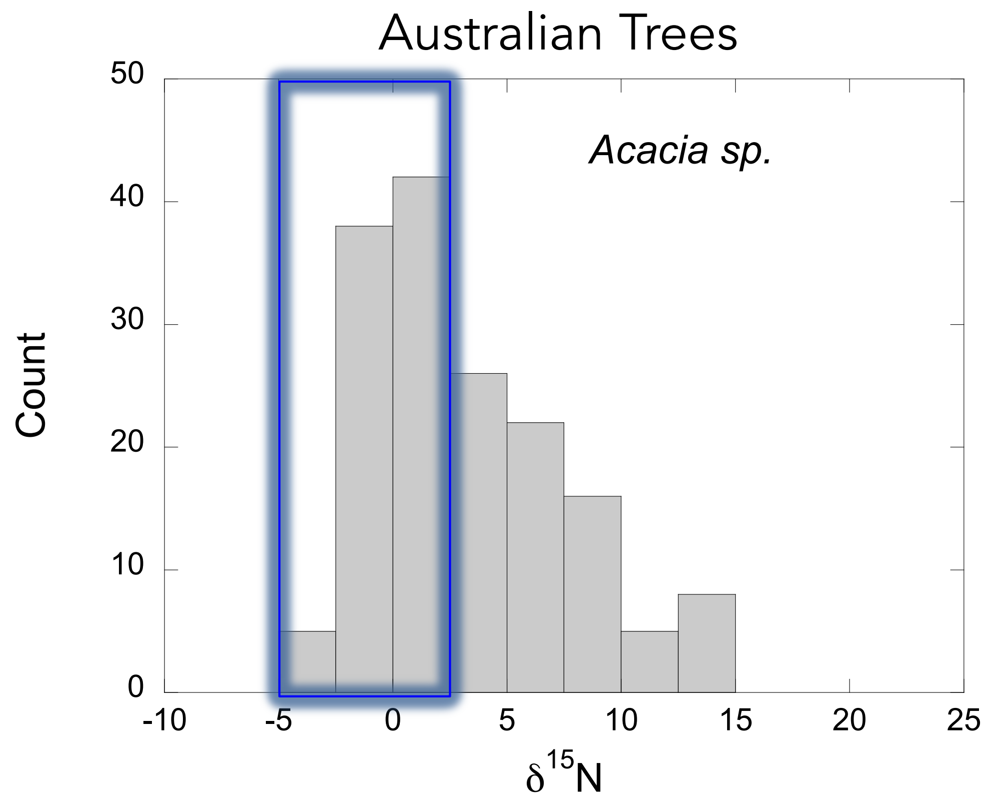


HN=NH	2)		1)	N_2
$H_2N{-}NH_2$	4)	(2X)	3)	HN=NH
$2NH_3$	6)		5)	$H_2N{-}NH_2$

$$N_2 + 8H^+ + 8e^- + 16\ ATP = 2NH_3 + H_2 + 16ADP + 16\ P_i$$

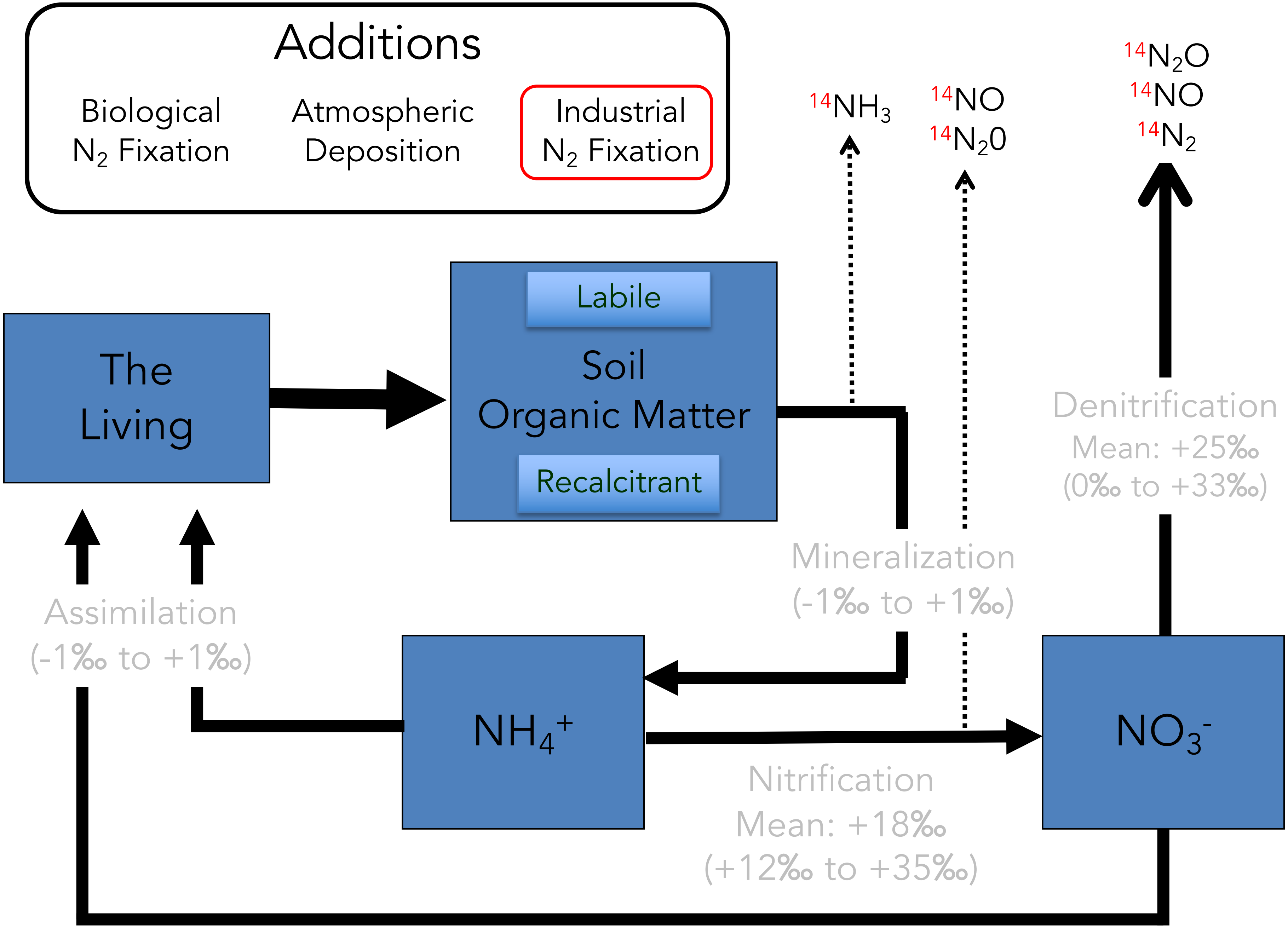
Discrimination During N_2 Fixation: 0‰ to -2‰



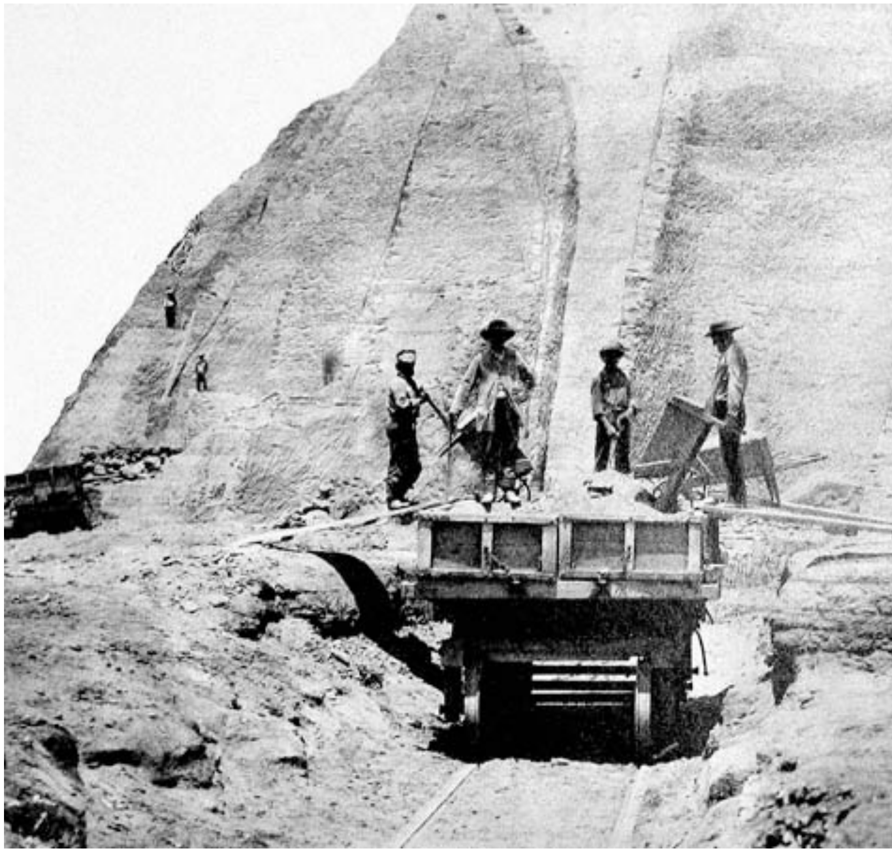


Nitrogen fixation is not perfect:

- Fixed nitrogen (NH_3) can be altered by fungi before plants assimilate it.
- Within plant fractionation (enzymatic or diffusion).
- Plants take up multiple sources (N_2/NH_4/NO_3)


Additions
Biological
N2 Fixation
Atmospheric
Deposition
Industrial
N2 Fixation
14NH3
14NO
14N20
14N2O
14NO
14N2
Labile
Soil
Organic Matter
Recalcitrant
The
Living
Denitrification
Mean: +25‰
(0‰ to +33‰)
Mineralization
(-1‰ to +1‰)
Assimilation
(-1‰ to +1‰)
NH4+
NO3-
Nitrification
Mean: +18‰
(+12‰ to +35‰)

Guano Wars: 1879–1883

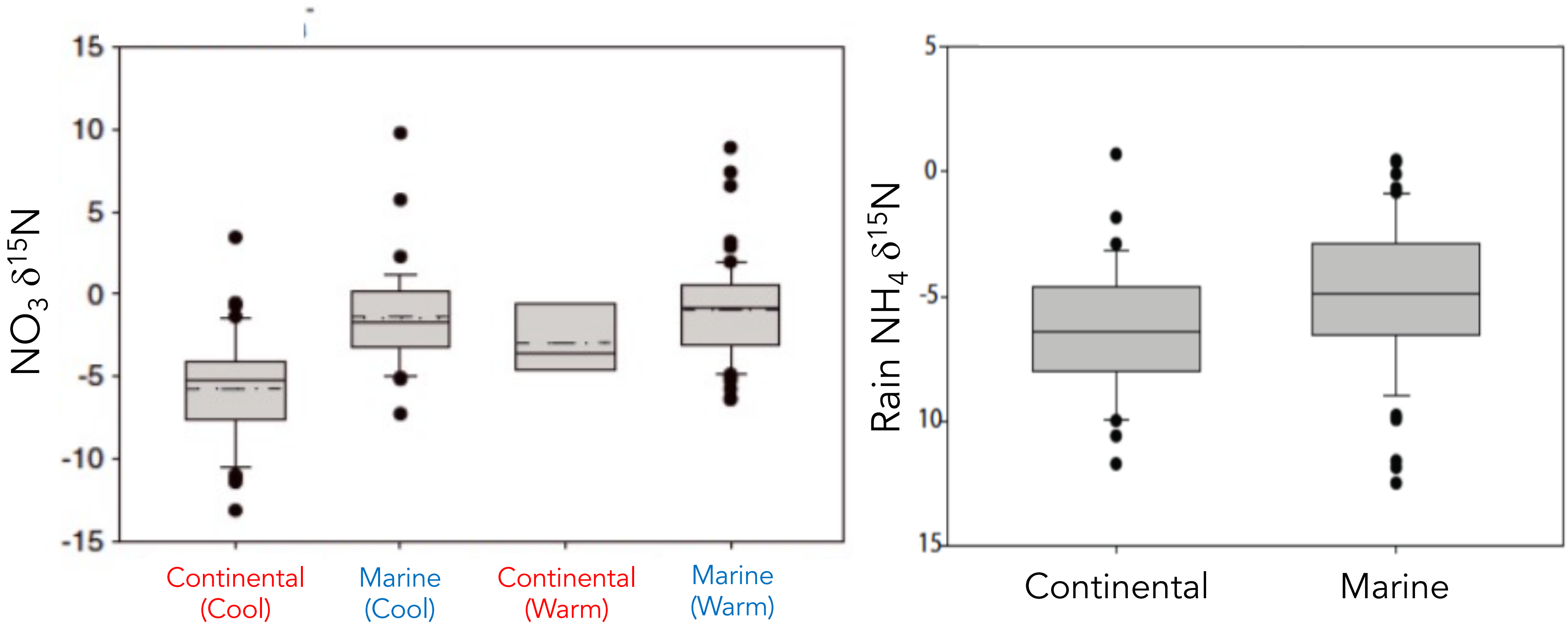


Productive Humboldt Current (Eastern Boundary Current).
Seabirds breed on offshore rocks absent of predators.
Seabird poo (guano): ammonium oxalate, urate, phosphates: high $\delta^{15}N$.
A rare but important commodity that created conflicts among countries.

Industrial N_2 Fixation

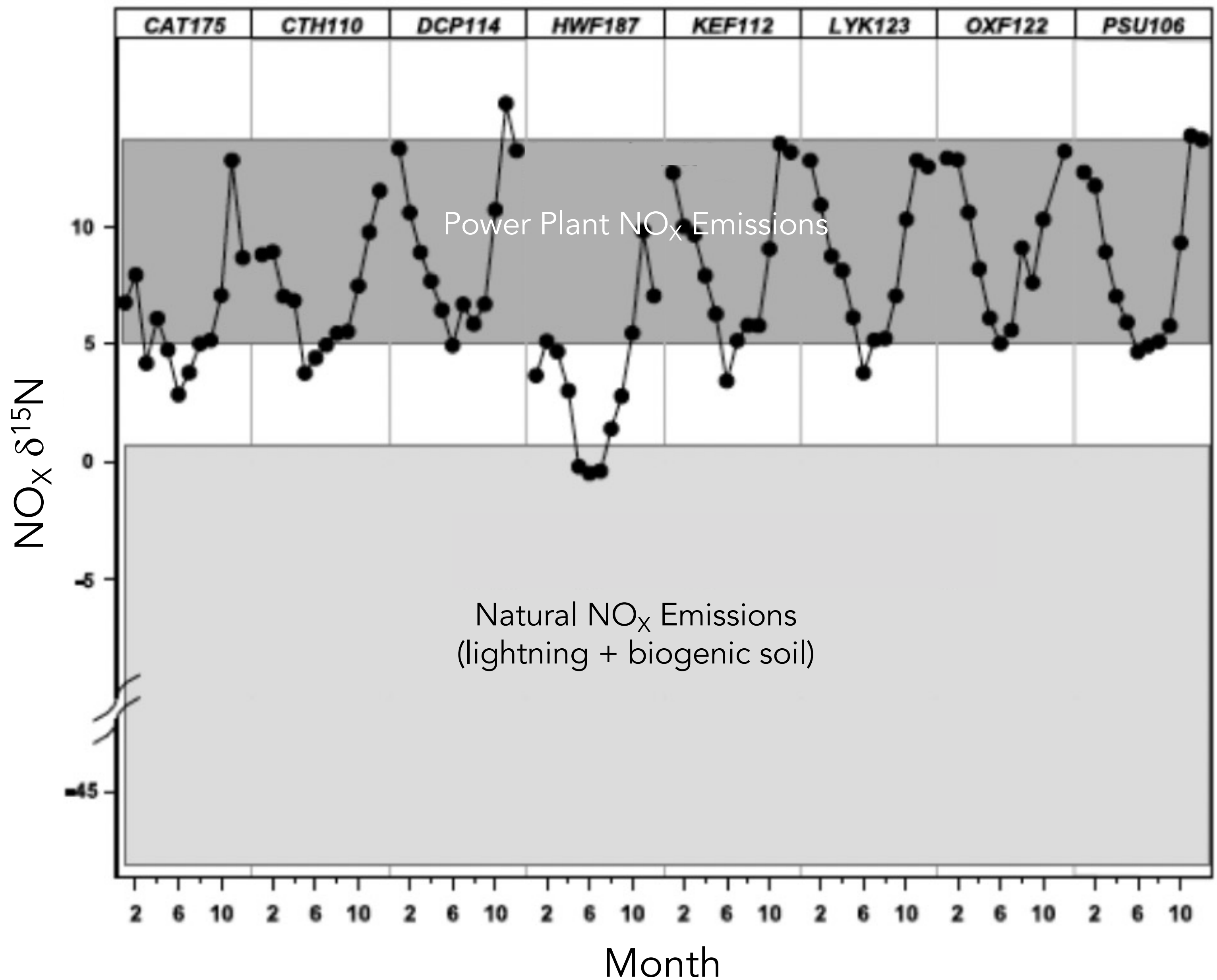
- Fritz Haber (1886–1934)
- 1918 Nobel Prize (Chemistry)
  - "Father of Chemical Warfare"
- Anthropogenic generation of fertilizers
  - >50% of current fertilizer production.
- Industrially completing the same reaction as biological N_2 fixation.
  - $2N + 3H_2 = 2NH_3$
- Fractionation close to zero but can vary by the process.
  Becomes progressively positive with processing.

Atmospheric Deposition

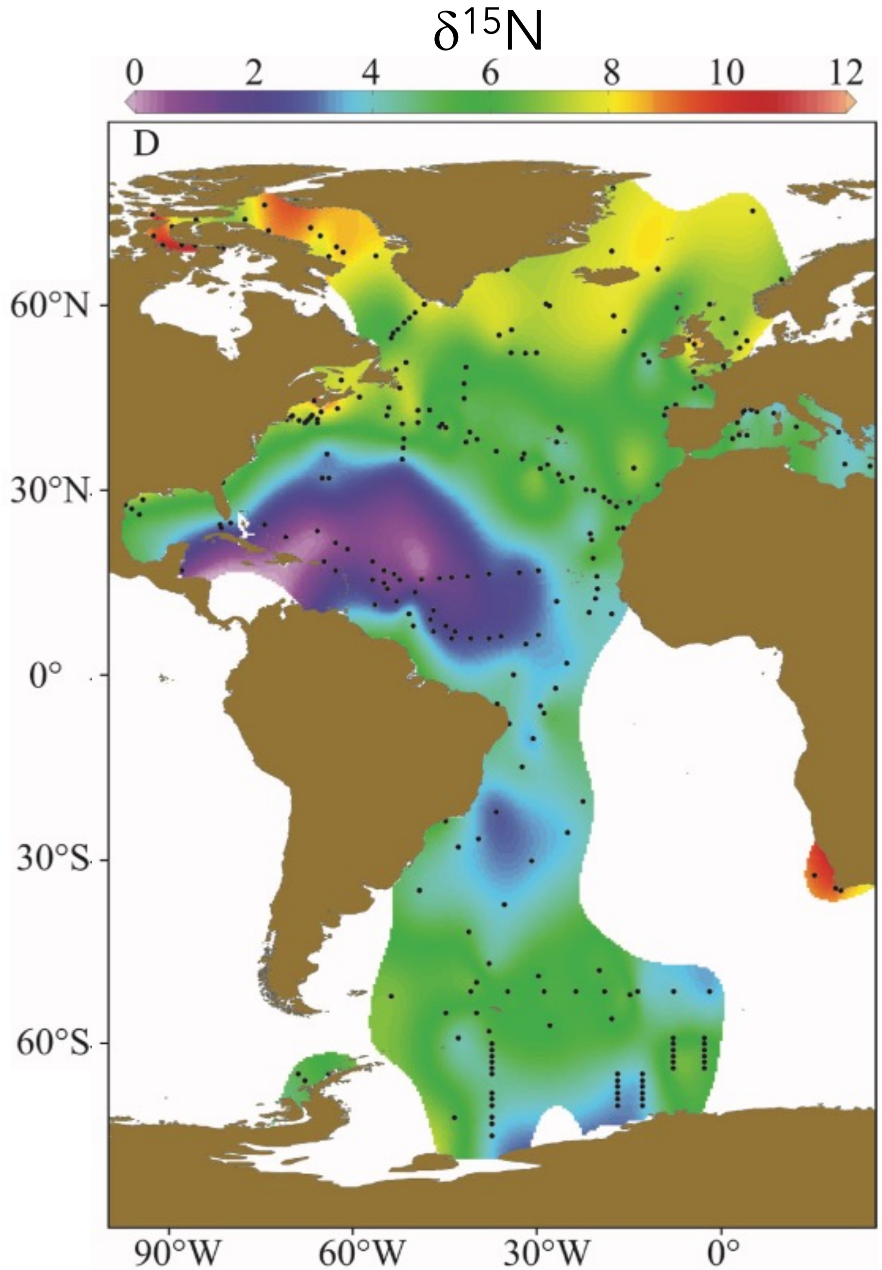


Altieri et al. 2013

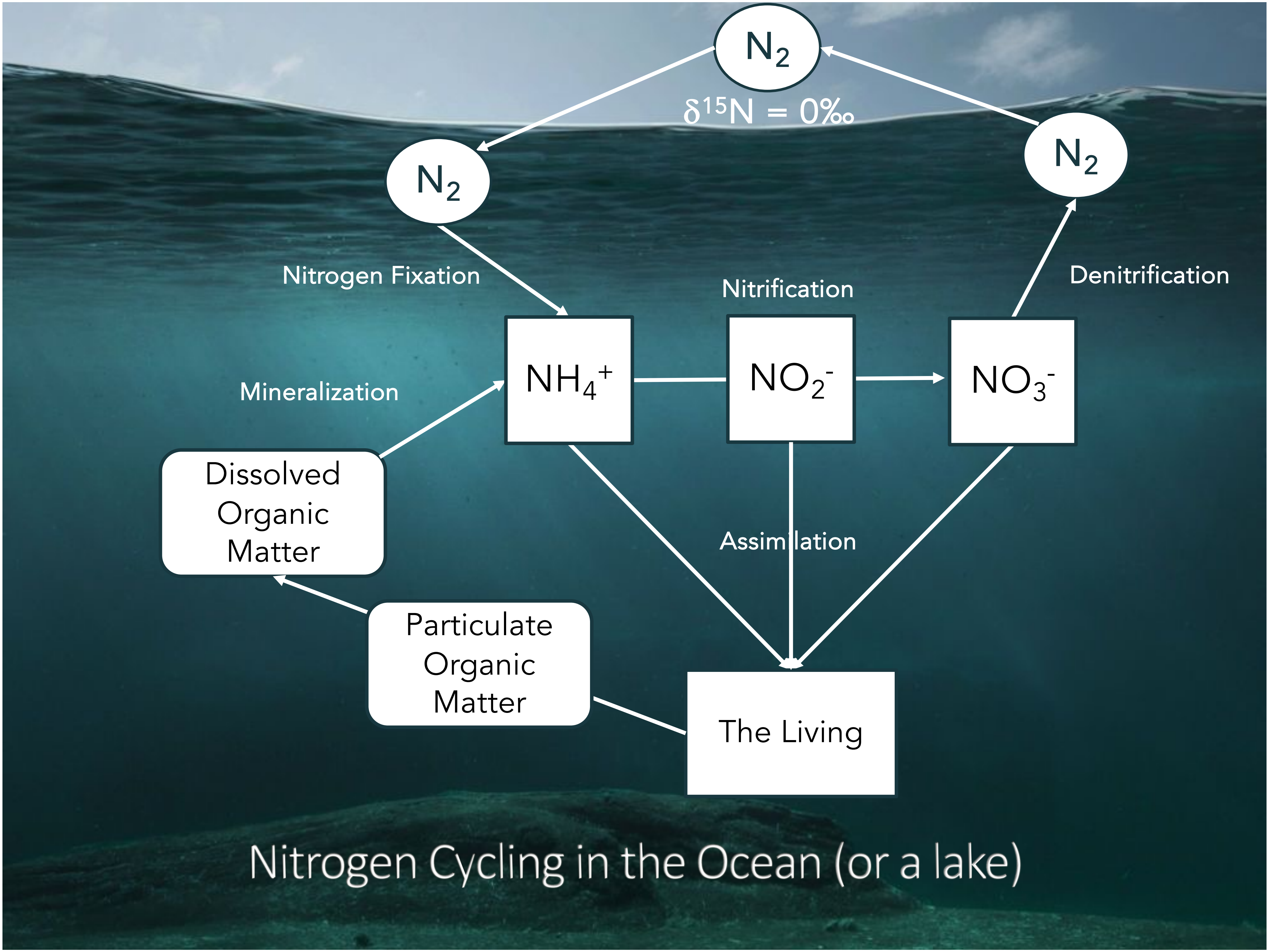
Power Plant NO_X Pollution



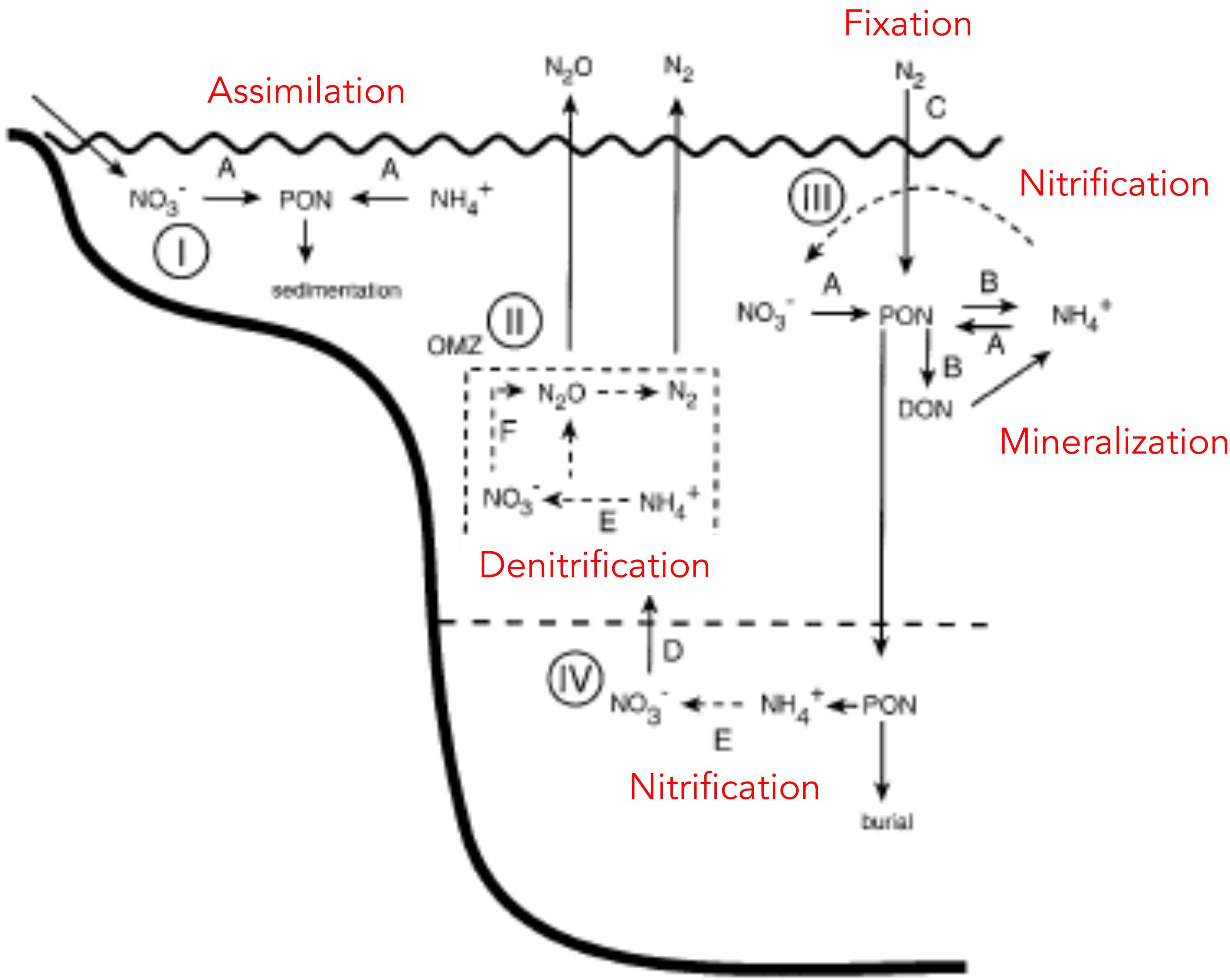
Primary Producer $\delta^{15}N$ Gradients in the Ocean



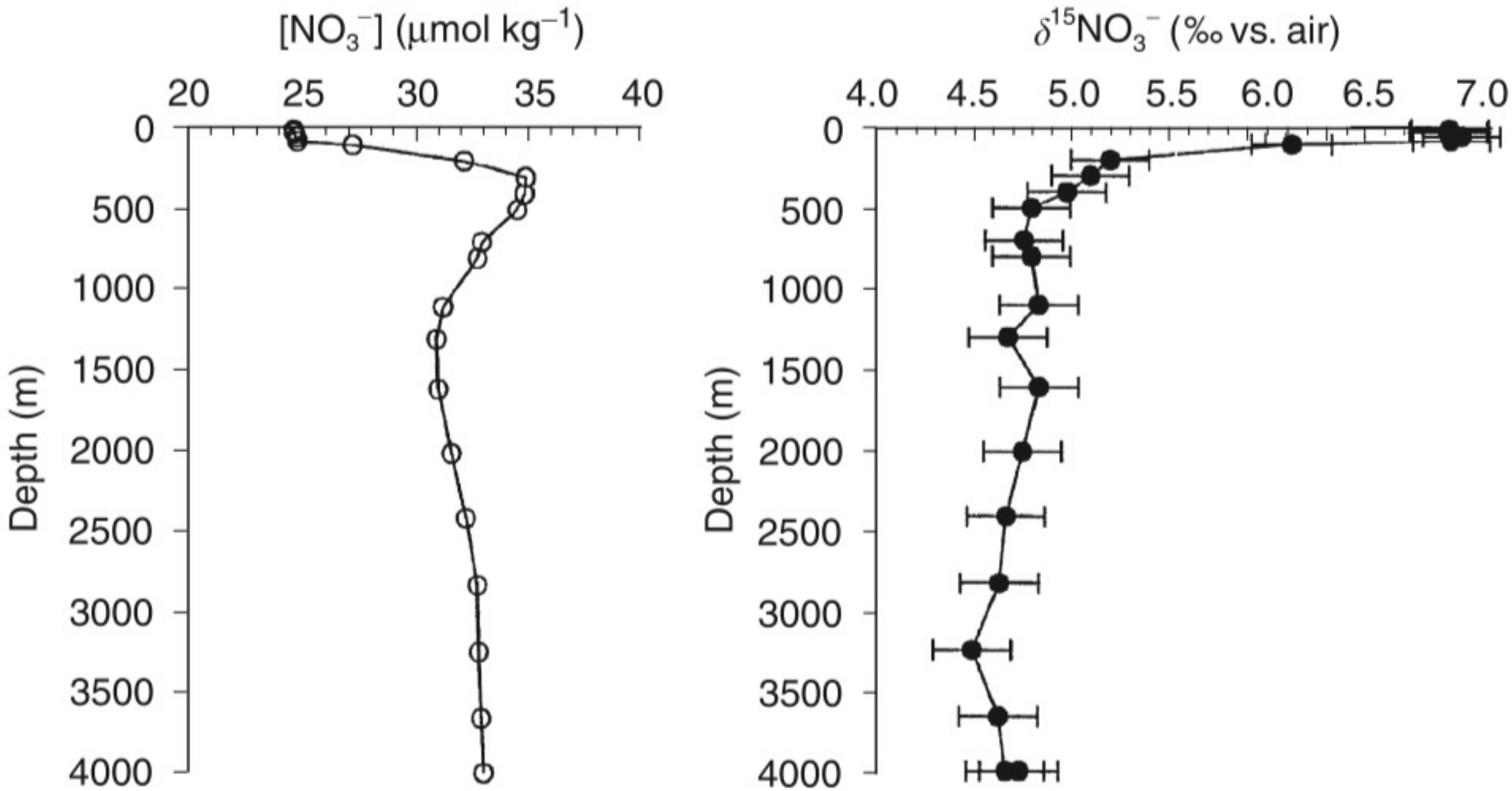
McMahon et al. 2013


N2
δ15N = 0‰
N2
N2
Nitrogen Fixation
Nitrification
Denitrification
NH4+
NO2-
NO3-
Mineralization
Dissolved Organic Matter
Assimilation
Particulate Organic Matter
The Living
Nitrogen Cycling in the Ocean (or a lake)

N Fractionating Processes Occur at Different Depths



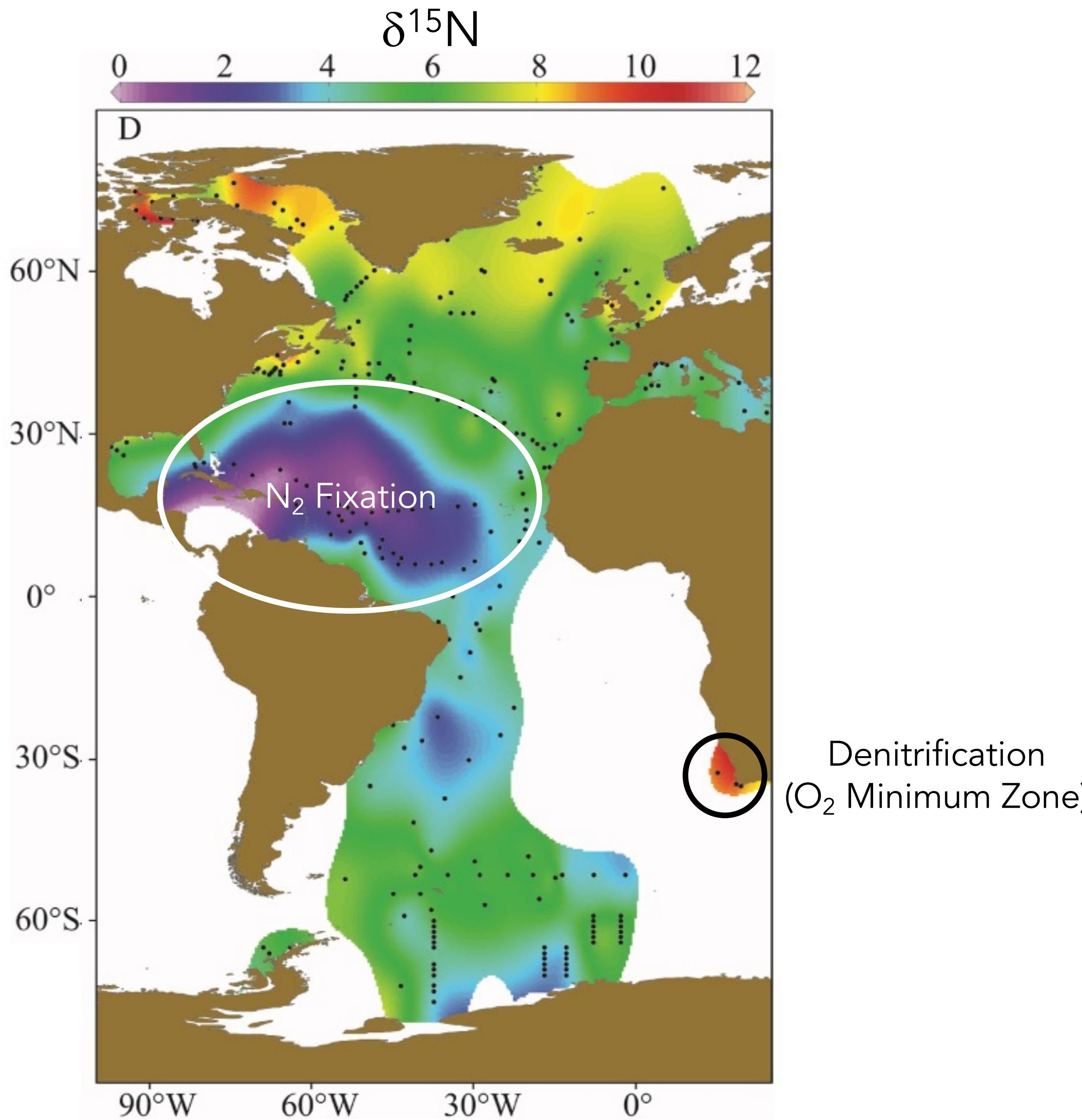
NO_3 Assimilation in Surface Ocean



Assimilation of NO_3^- by primary producer strongly influences the $\delta^{15}N$ value of the remaining dissolved NO_3^-

Sigman, Karsh, and Casciotti 2011

Primary Producer $\delta^{15}N$ Gradients in the Ocean



McMahon et al. 2013

N_2 Fixation in the Oligotrophic Pacific Ocean