



Fertilisation azotée de l'océan primitif par des microorganismes continentaux à l'Archéen ?

Thomazo C, Couradeau E, Garcia-Pichel F

INTRODUCTION

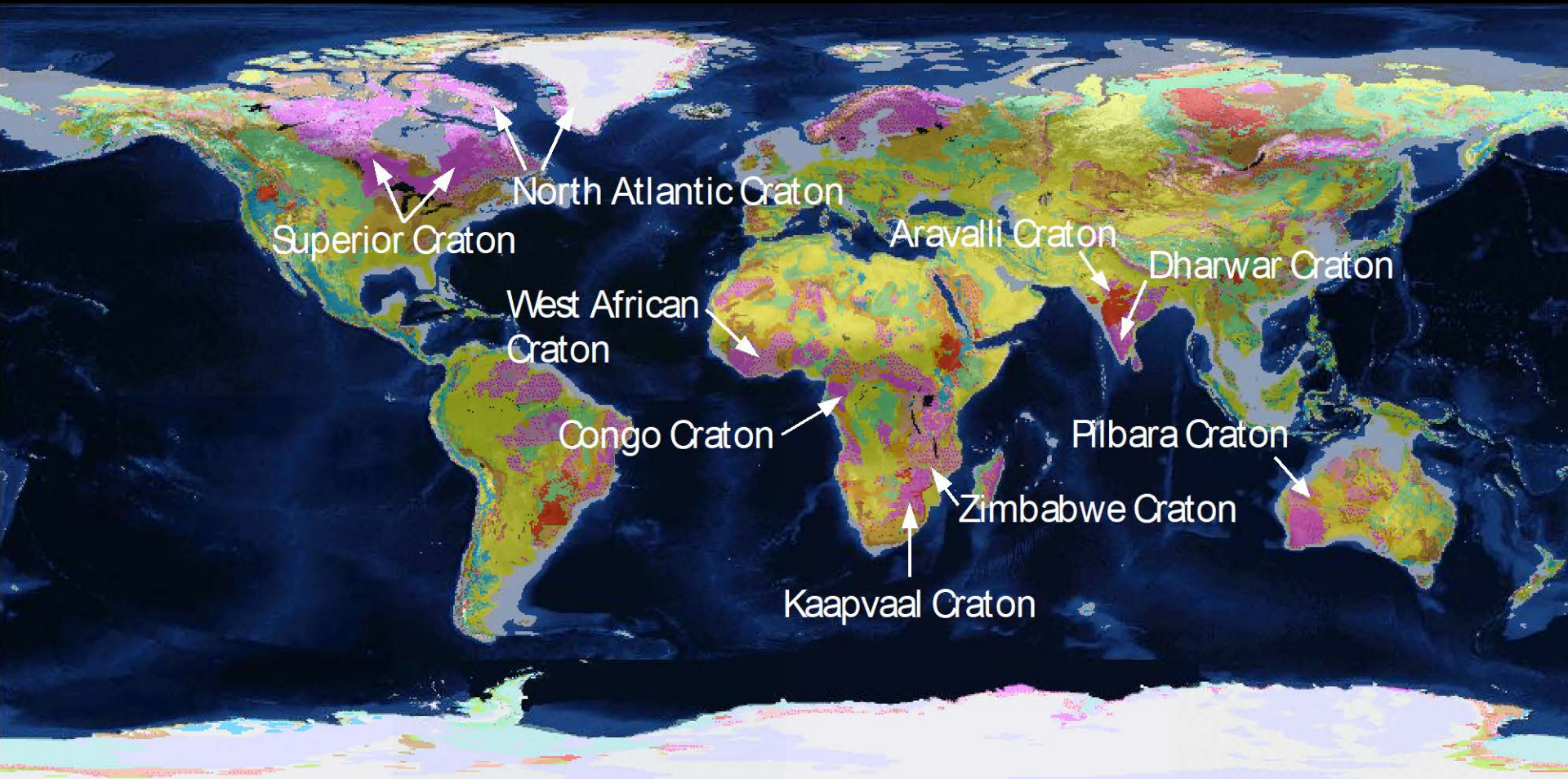
	Eonothem Eon	Erathem Era	System Period	Age Ma	GSSP GSSA
Precambrian	Proterozoic	Neo-proterozoic	Ediacaran	542	
			Cryogenian	~635	🔑
			Tonian	850	🔄
		Meso-proterozoic	Stenian	1000	🔄
			Ectasian	1200	🔄
			Calymmian	1400	🔄
		Paleo-proterozoic		1600	🔄
			Statherian	1800	🔄
			Orosirian	2050	🔄
			Rhyacian	2300	🔄
			Siderian	2500	🔄
	Archean	Neoarchean		2800	🔄
		Mesoarchean		3200	🔄
		Paleoarchean		3600	🔄
		Eoarchean		4000	
	Hadean (informal)			~4600	



- Ocean formation
- **Oxidation of the environment**
Ocean and Atmosphere
- Continental crustal growth
- **Development of life**

~ Half of the geological record

INTRODUCTION



... BUT Poorly archived, few sediments most of them deposited after 3.5 Ga, **metamorphism to at least 200°C**

INTRODUCTION

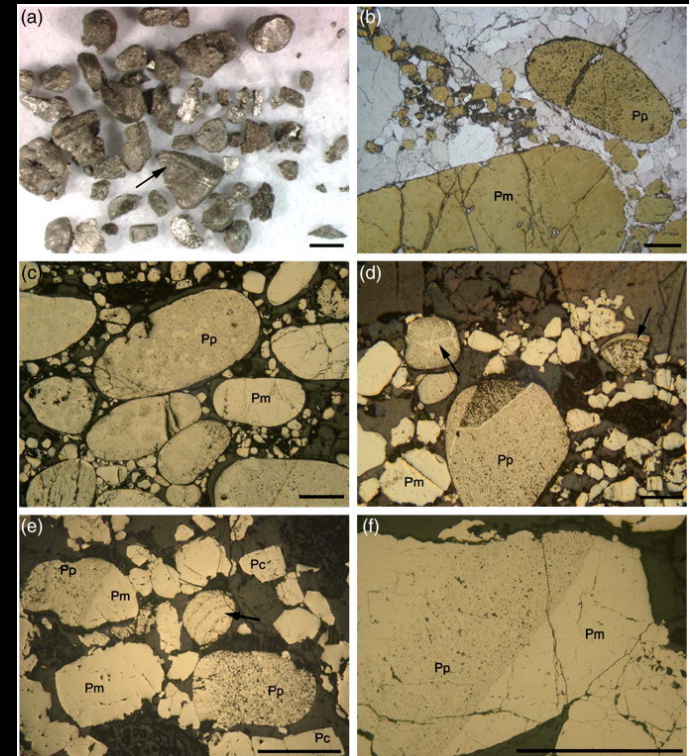
The records of Earth oxygenation

1/ Looks for the chemistry of sedimentary deposits (ox or red)

Banded Iron Formation



Detrital pyrites

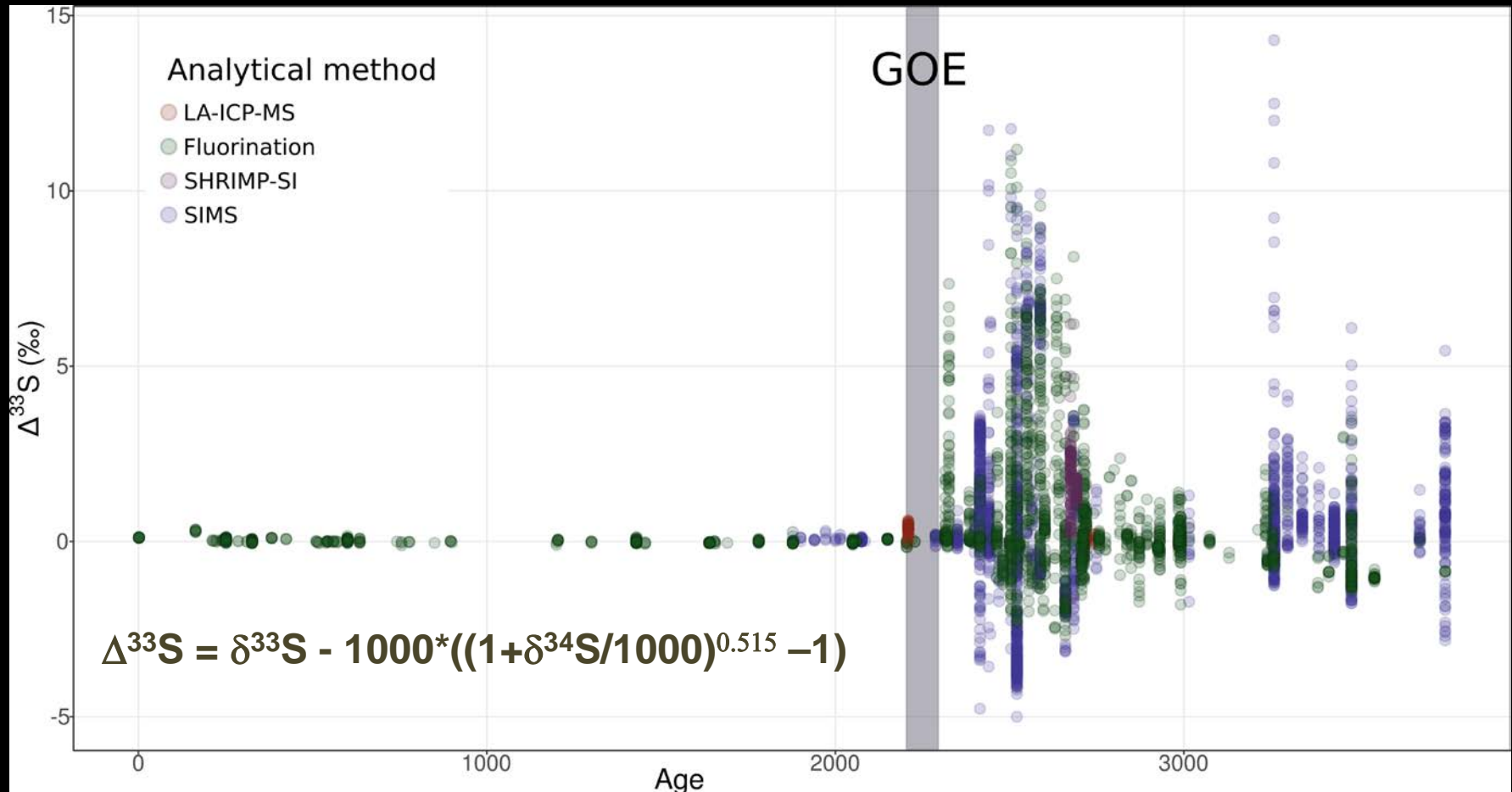


Hofmann et al., 2009

INTRODUCTION

The records of Earth oxygenation

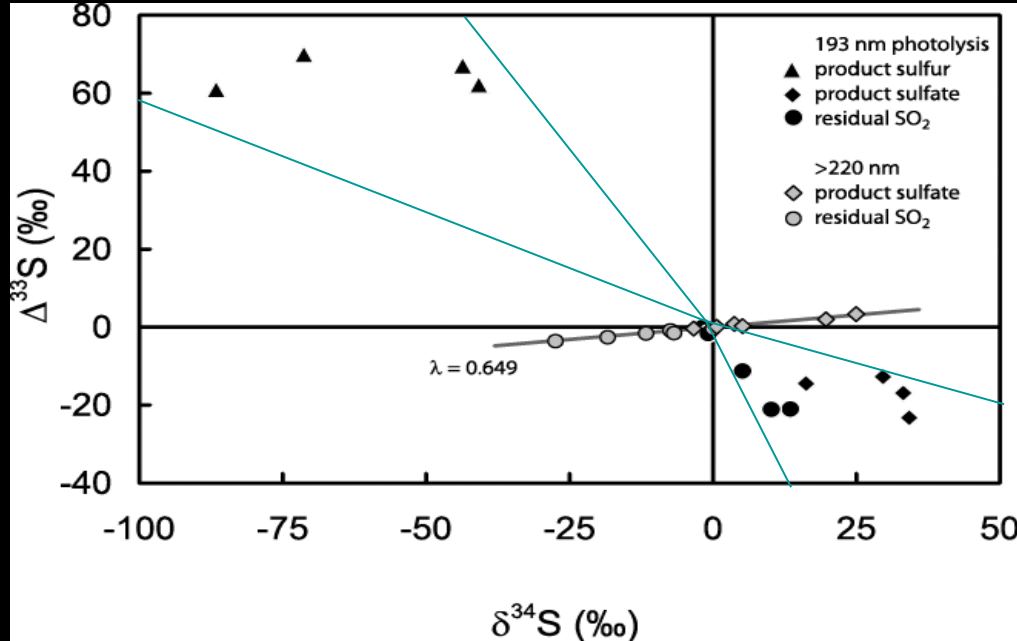
- 1/ Looks for the type of sedimentary deposit (ox or red)
- 2/ Looks for chemical signature of oxygen in the ocean / atmosphere



INTRODUCTION

The records of Earth oxygenation

- MIF-S are produced in lab experiment during UV photolysis of SO_2



Farquhar et al., 2000



Photolytic reaction of S in
anoxic atmosphere

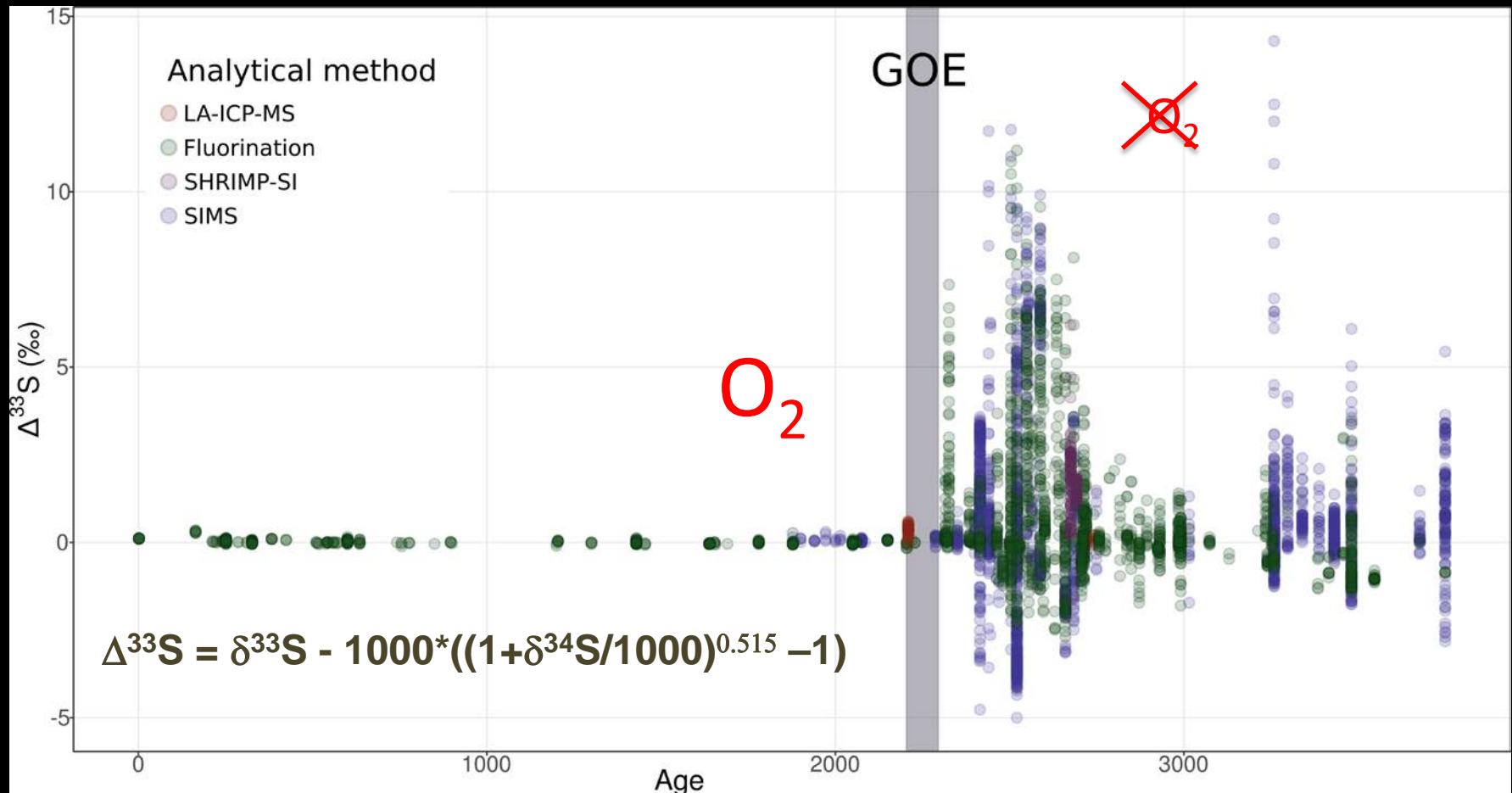


Without O_2 (O_3)

INTRODUCTION

The records of Earth oxygenation

- 1/ Looks for the type of sedimentary deposit (ox or red)
- 2/ Looks for chemical signature of oxygen in the ocean / atmosphere



INTRODUCTION

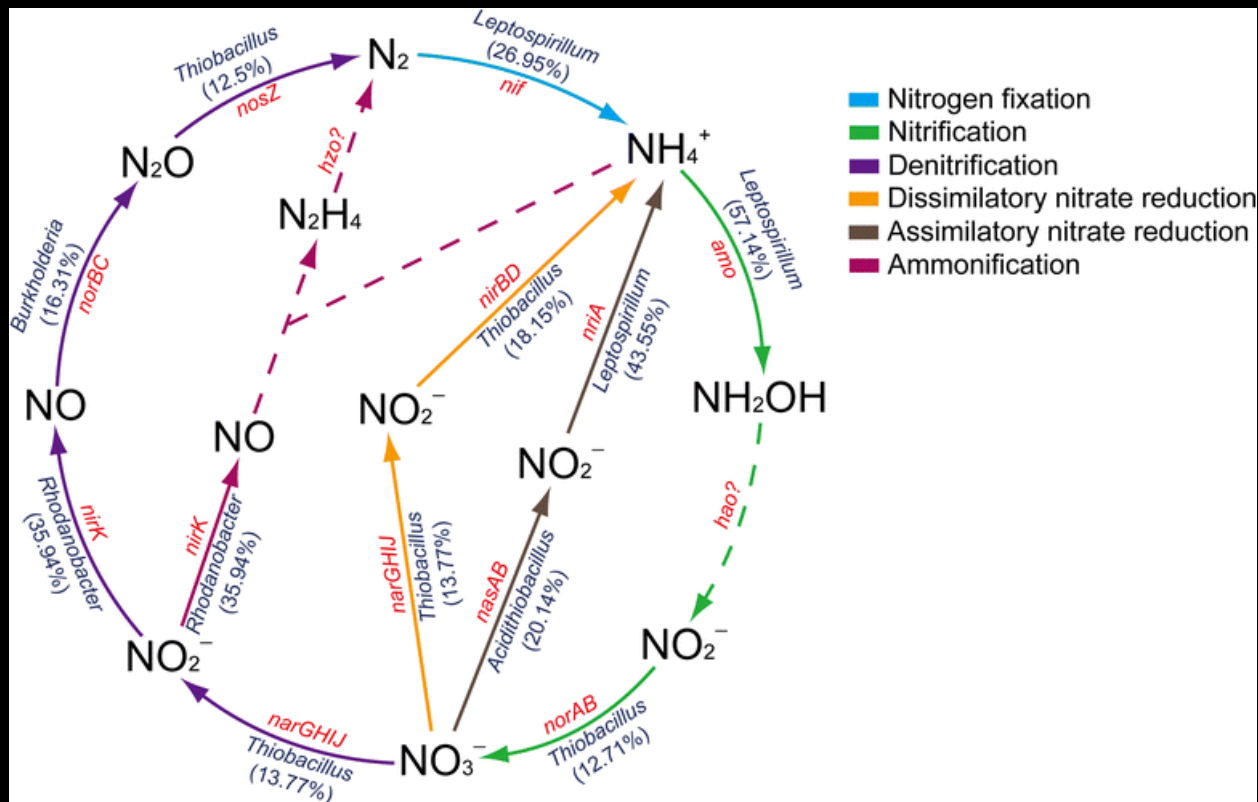
The records of Earth oxygenation

- 1/ Looks for the type of sedimentary deposit (ox or red)
- 2/ Looks for chemical signature of oxygen in the ocean / atmosphere
- 3/ Looks for biological record of metabolisms performing respiration (O_2 but also sulfate, **nitrate**, iron oxides etc.)

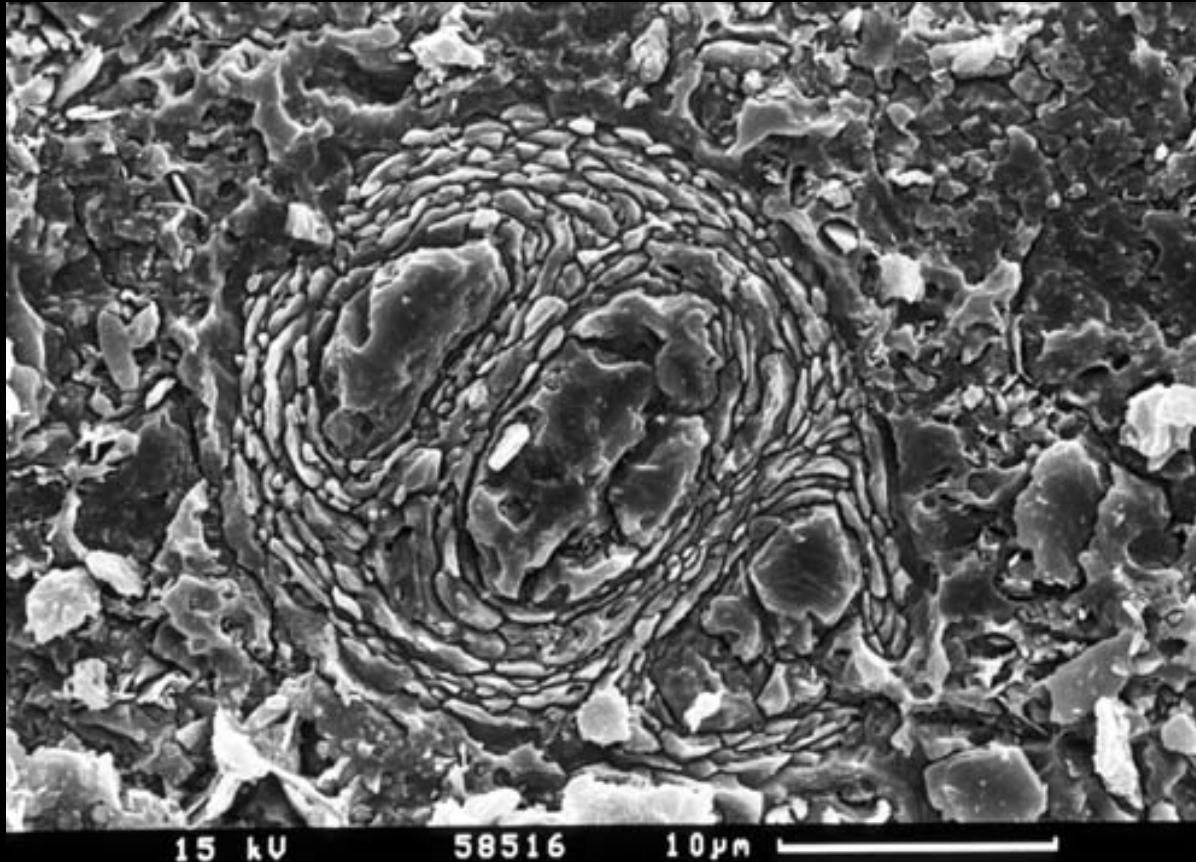
Type	Lifestyle	Electron acceptor	Products	E_o' [V]	Example organisms
Aerobic respiration	Obligate and facultative aerobes	O_2	$H_2O + CO_2$	+0.82	eukaryotes and aerobic prokaryotes
Nitrate reduction	Facultative aerobes	nitrate (NO_3^-)	nitrite (NO_2^-)	+0.40	<i>E.coli</i>
Fumarate respiration	Facultative aerobes	fumarate	succinate	+0.03	<i>E.coli</i>
Sulfate respiration	Obligate anaerobes	sulfate (SO_4^{2-})	sulfide (HS^-)	-0.22	<i>Desulfobacter latus</i>
Sulfur respiration	Facultative aerobes and obligate anaerobes	sulfur (S^0)	sulfide (HS^-)	-0.27	<i>Desulfuromonadales</i>

INTRODUCTION

Early Earth Nitrogen metabolisms ?



INTRODUCTION



Unknown Paleozoic microfossil probably related to *O. duoportius*
(SEM image, etched rock surface) - *credit Axel Munnecke*

... most of the time organic remain are difficult to recognize
and classify ... though chemical reaction is unknown

INTRODUCTION



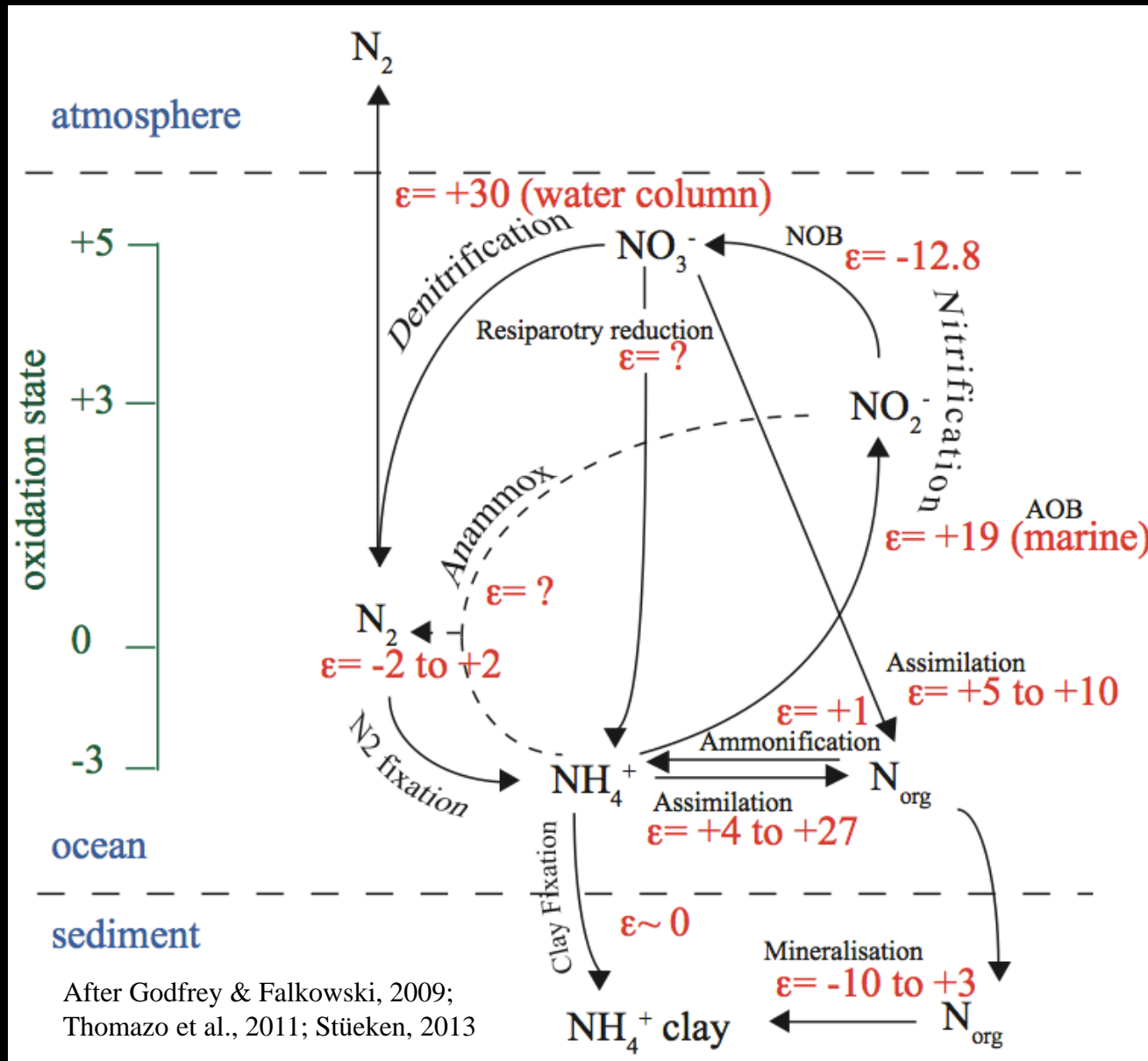
Stable isotopes are used to trace:

The origin of organic remains (because life tends to exert strong fractionation compared to abiotic reaction).

Different metabolic activities = different fractionations and byproducts precipitating as biominerals.

Moreover, Secondary alterations can be tested in most cases (*Rayleigh distillation model*).

Lessons from the modern N cycle

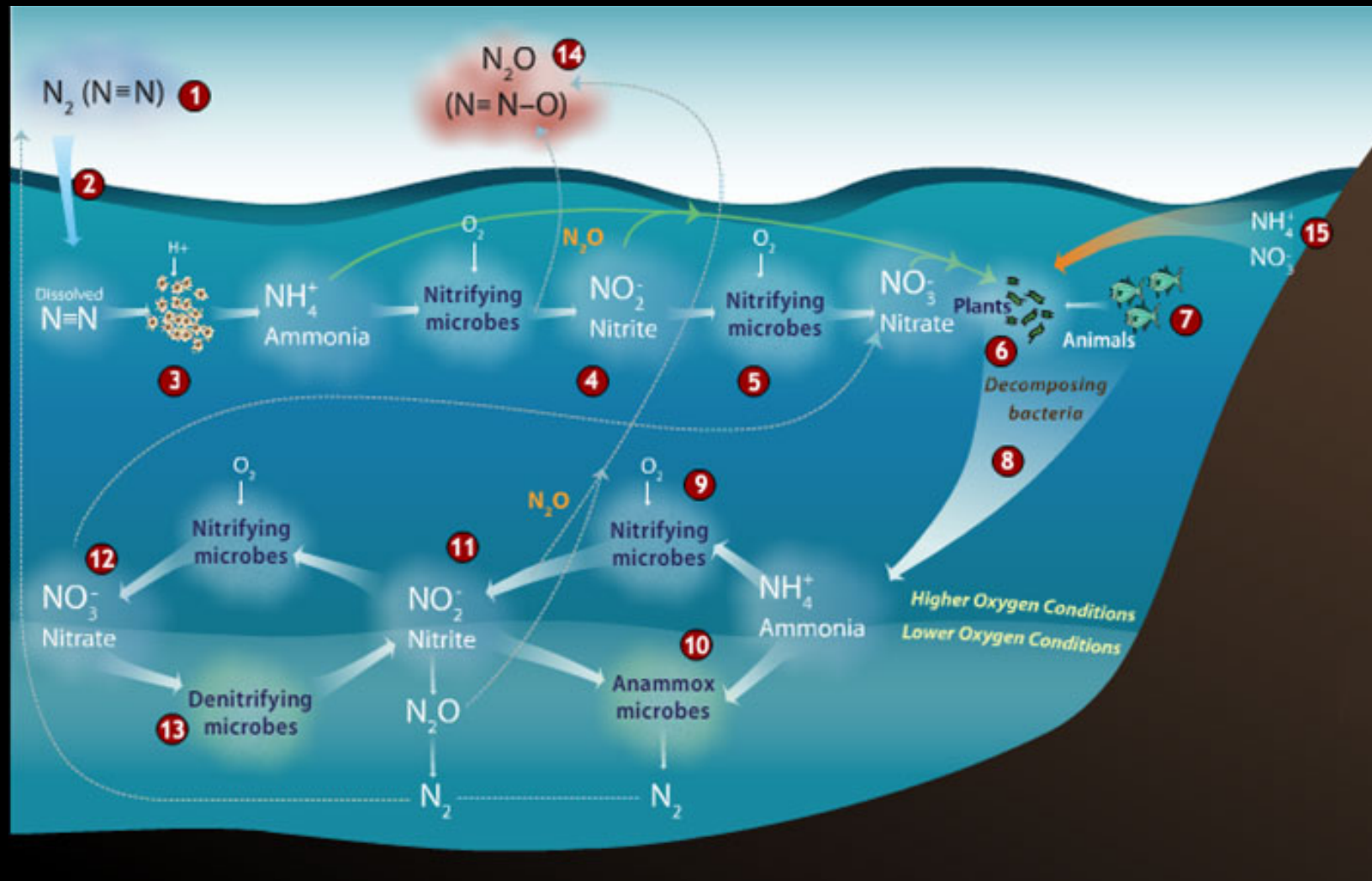


N is one of the major nutrients

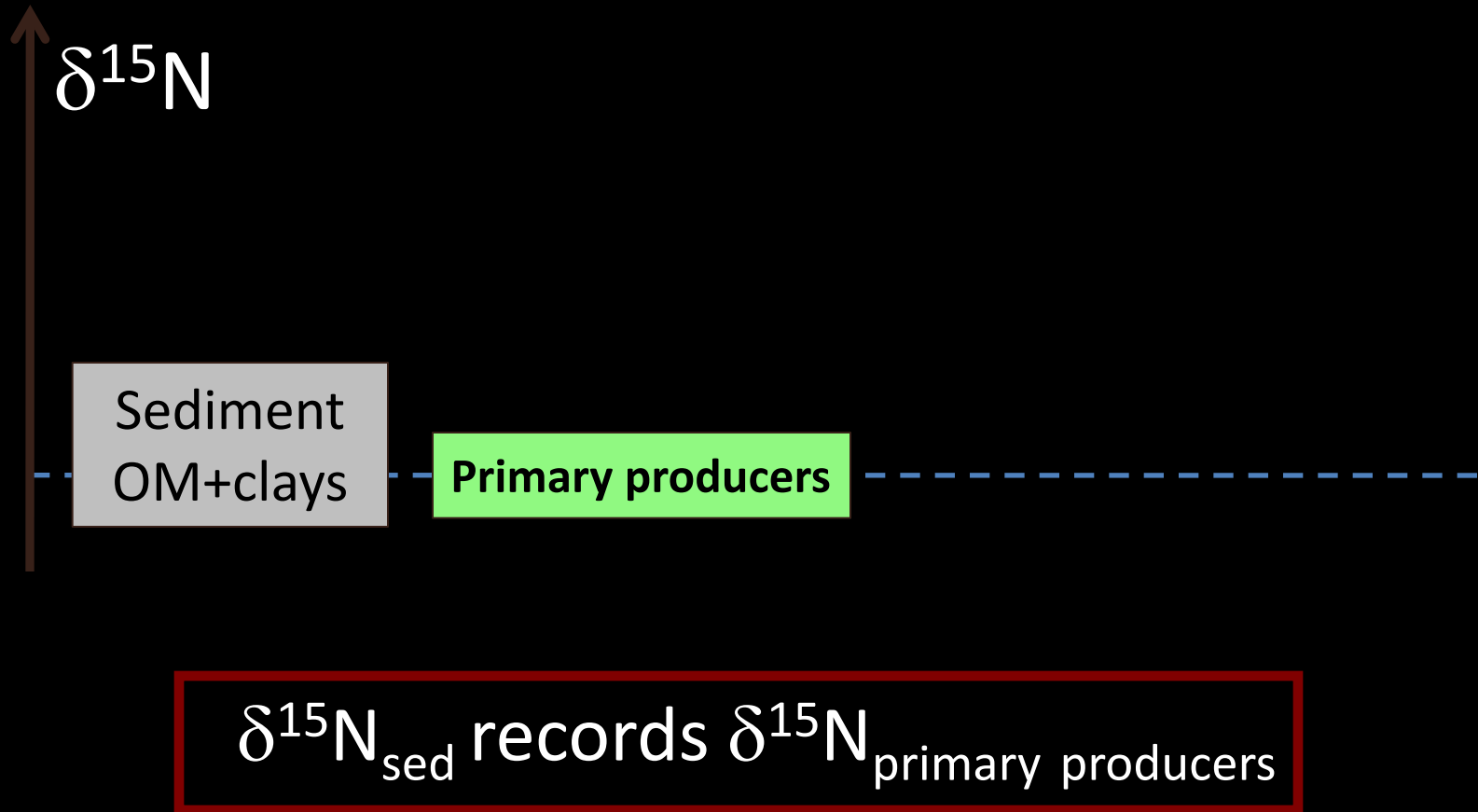
=> The N cycle interacts strongly with primary productivity

The N cycle is mediated by redox reactions

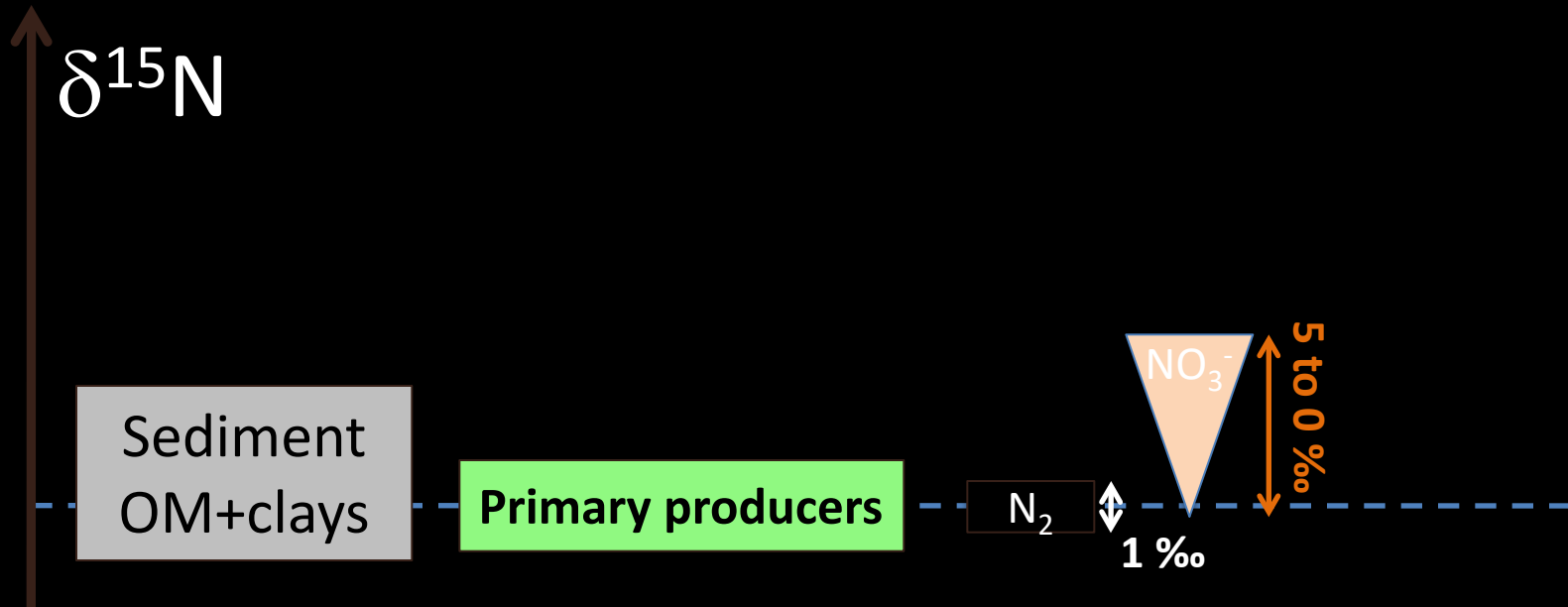
Lessons from the modern N cycle



Lessons from the modern N cycle

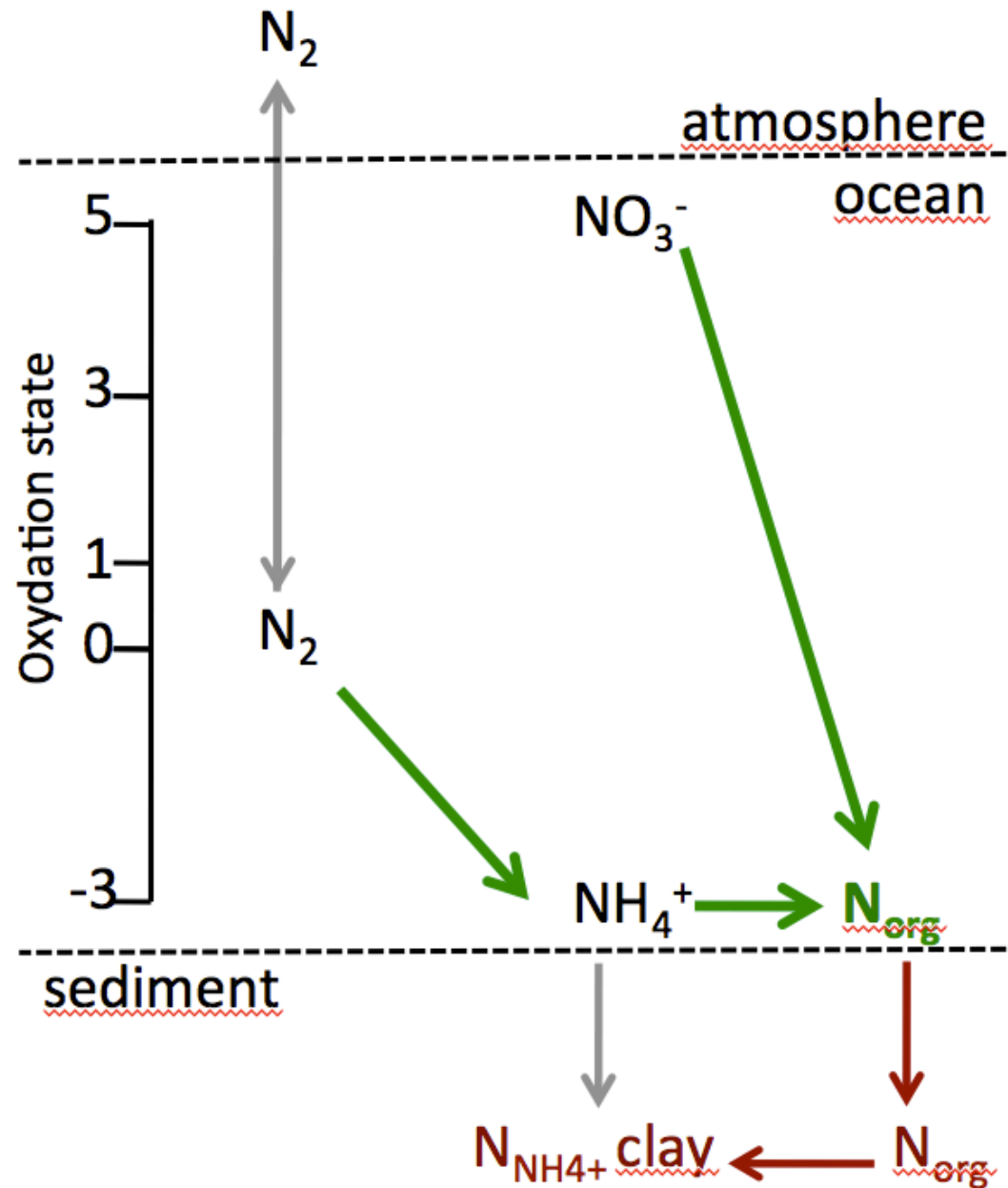


Lessons from the modern N cycle



$\delta^{15}\text{N}_{\text{primary producers}}$ records nitrogen sources $\delta^{15}\text{N}$

Lessons from the modern N cycle

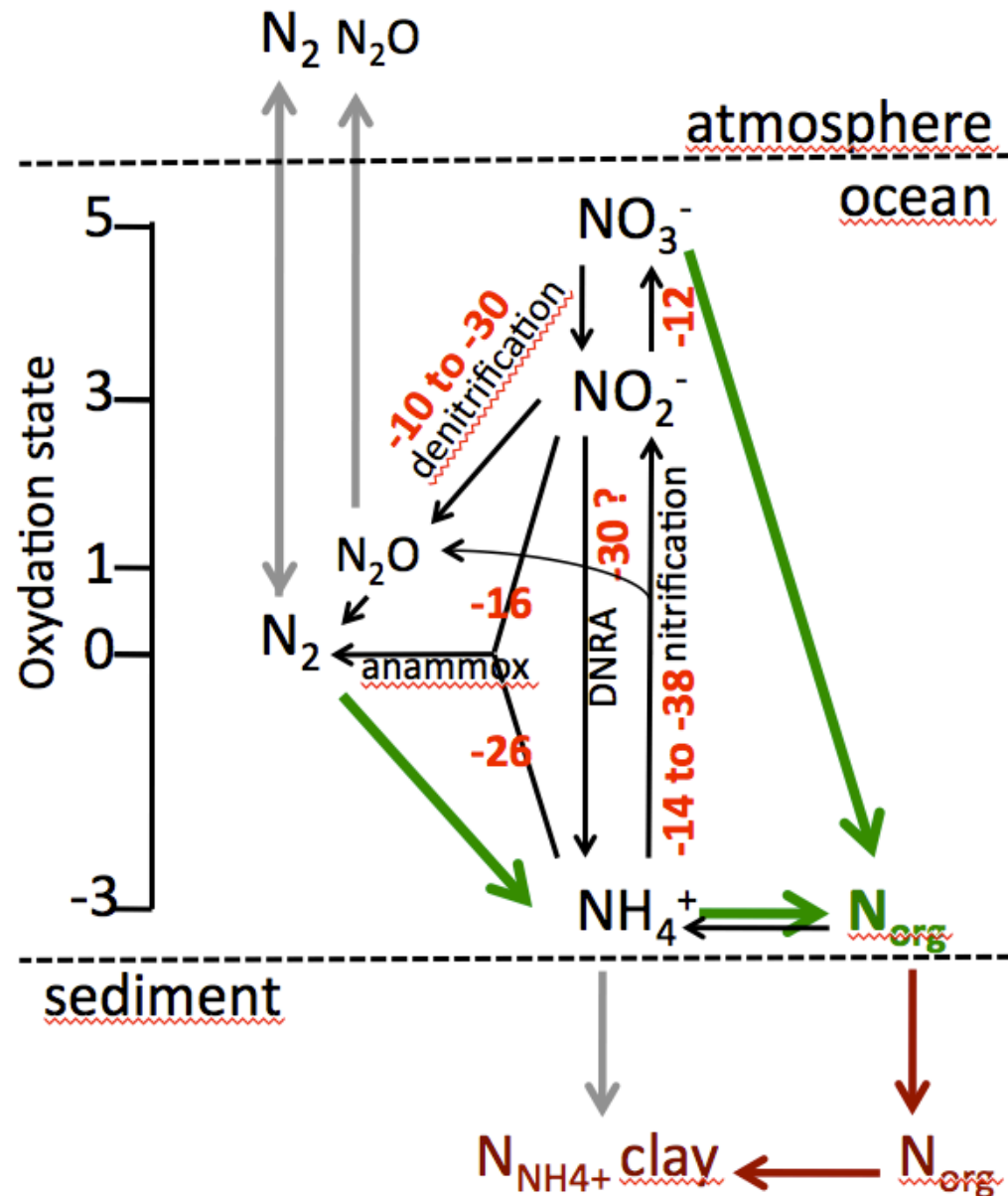


Lessons from the modern N cycle

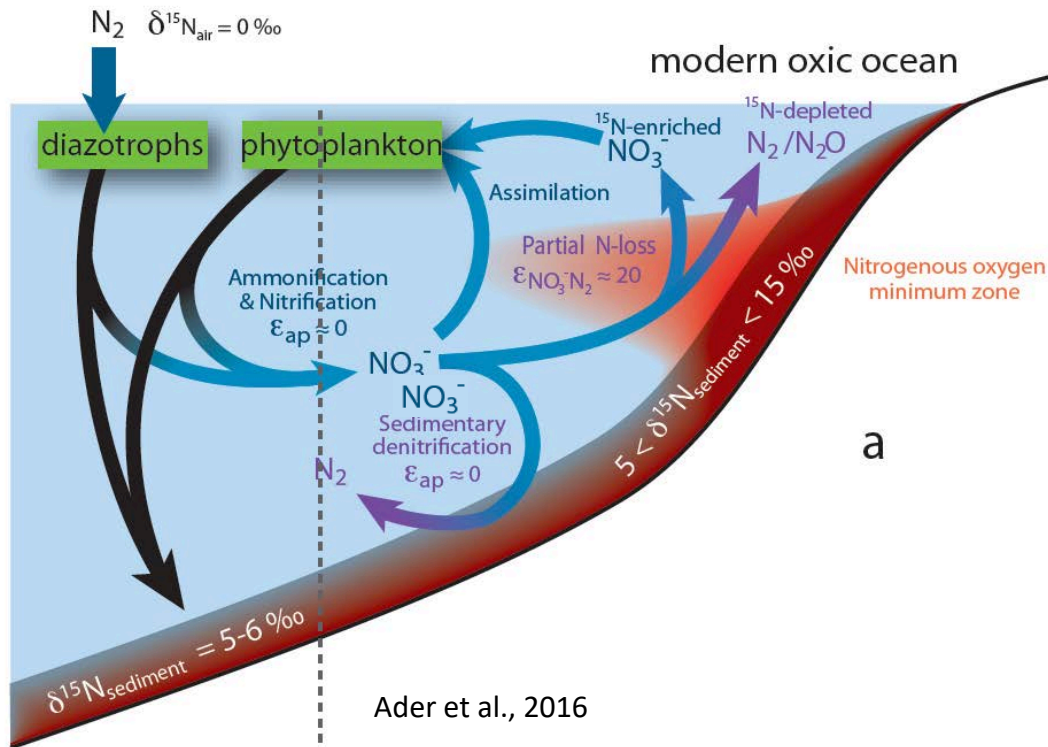
$$\epsilon = \delta^{15}\text{N}_{\text{product}} - \delta^{15}\text{N}_{\text{reactant}}$$

! Can be expressed only
when the reaction is not
quantitative !

The $\delta^{15}\text{N}$ of
nitrogen sources
depend on how
the nitrogen
cycle operates

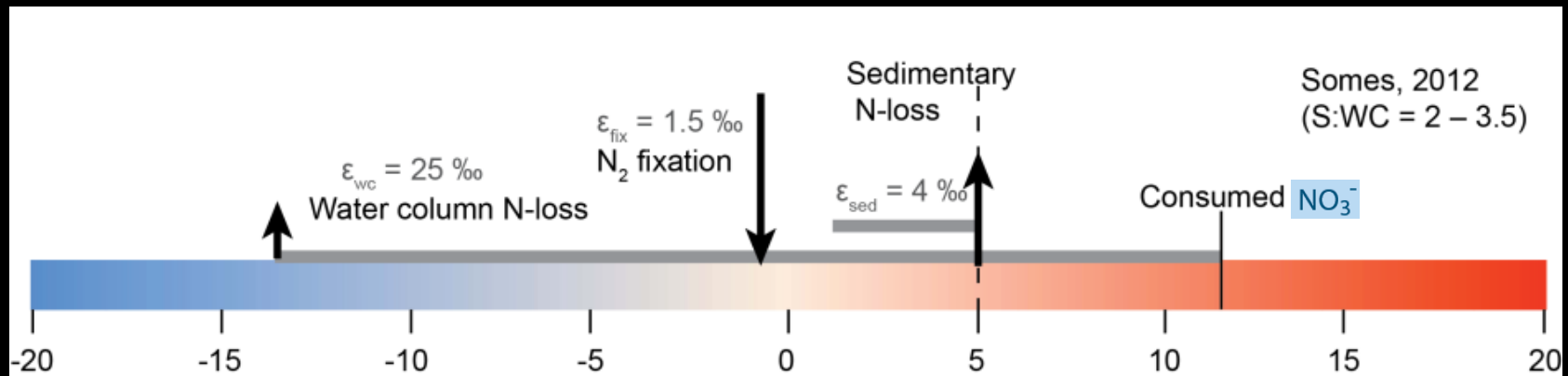


Lessons from the modern N cycle

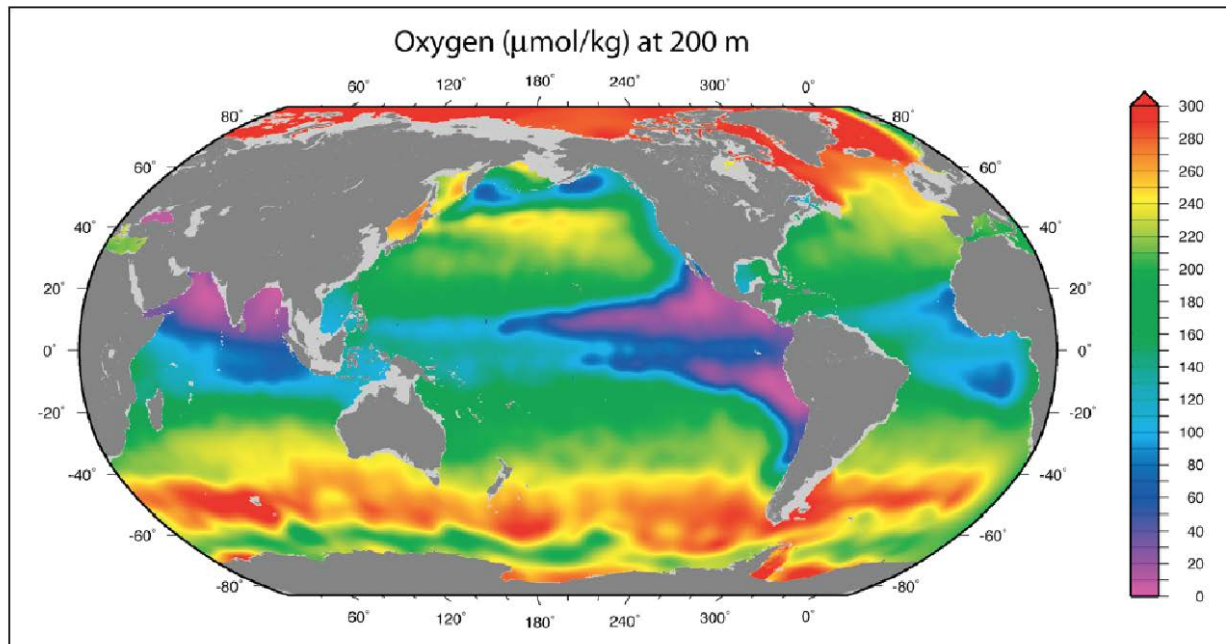
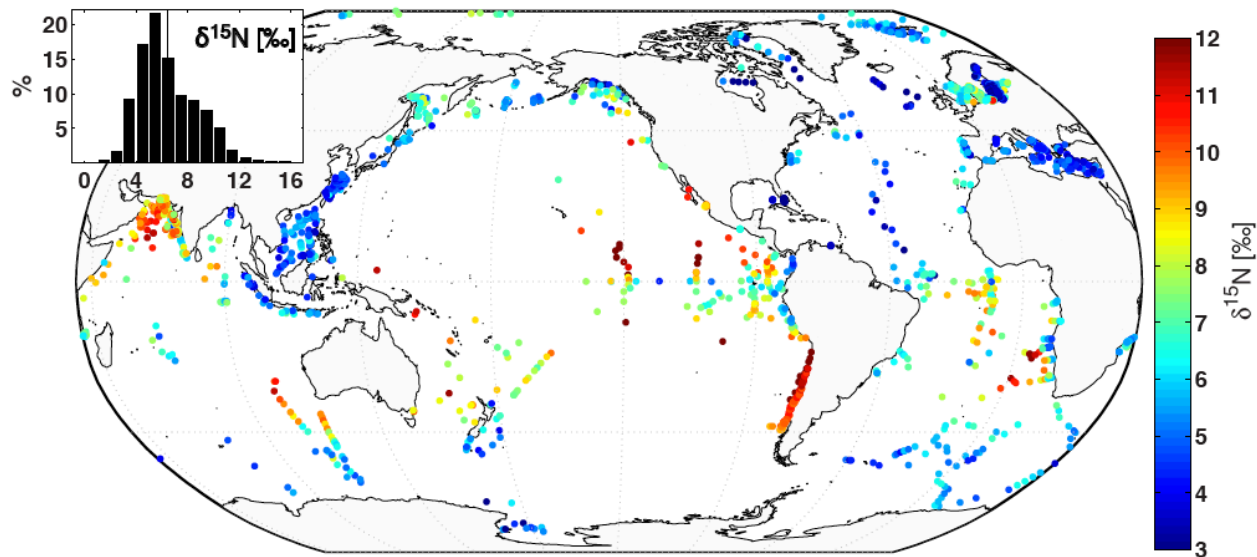


$\delta^{15}N$ is controlled by the balance of nitrogen fixation and denitrification

All the Phanerozoic record can be interpreted like this (e.g. Algeo et al. 2014)

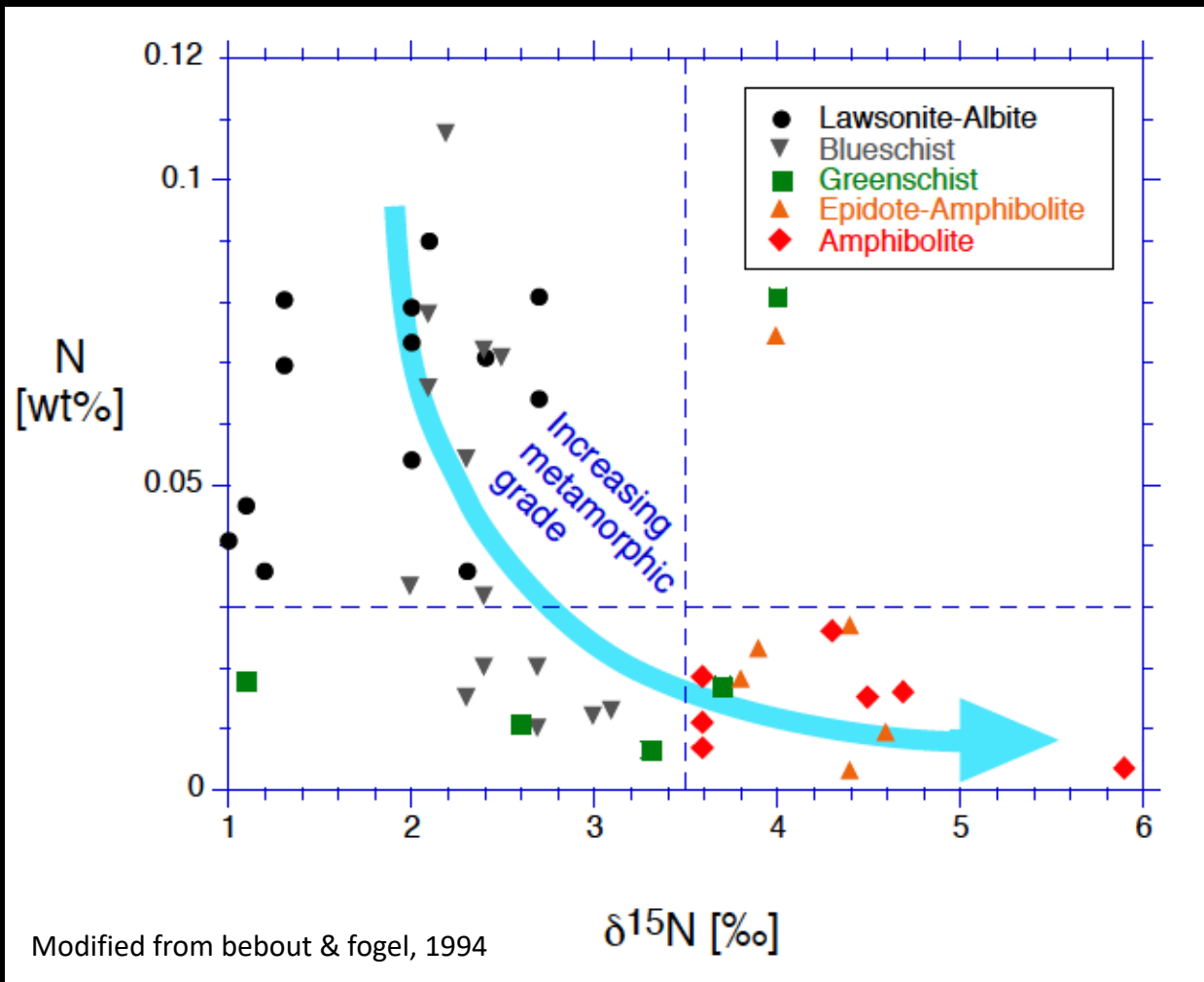


Lessons from the modern N cycle

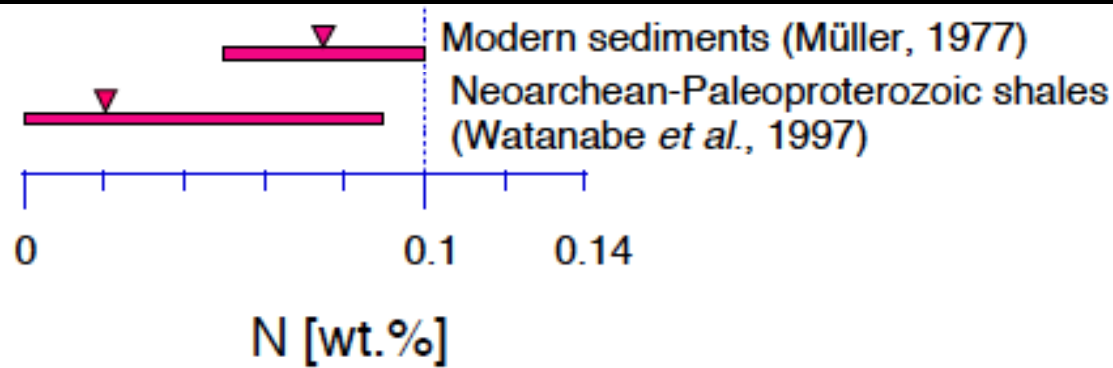


Early Earth complications

* Sedimentary N content and $\delta^{15}\text{N}$ evolve with metamorphism

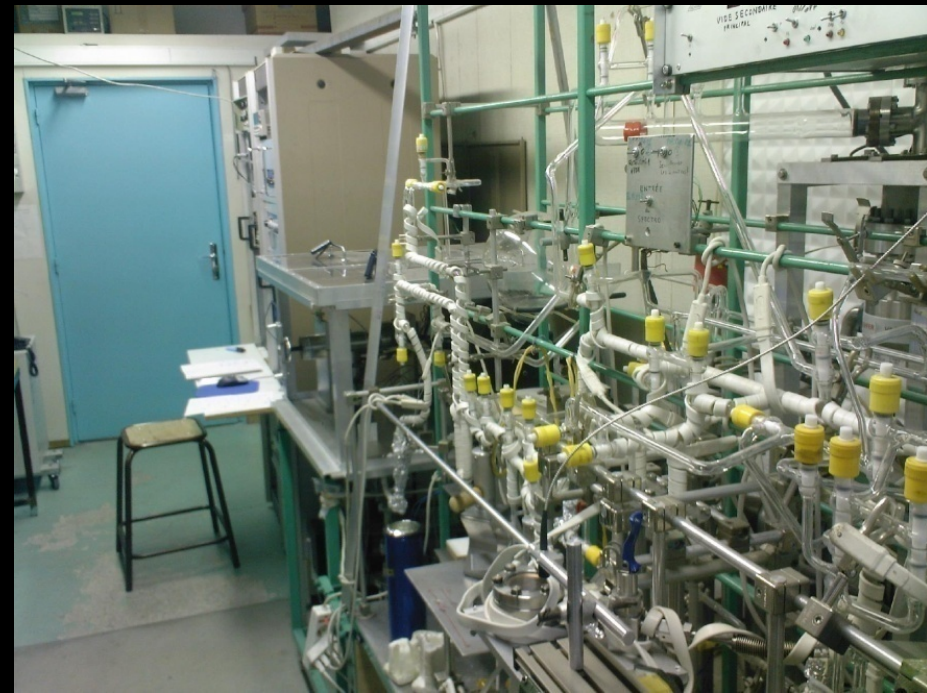


Early Earth complications



Static mass spectrometer instrument (IPGP)

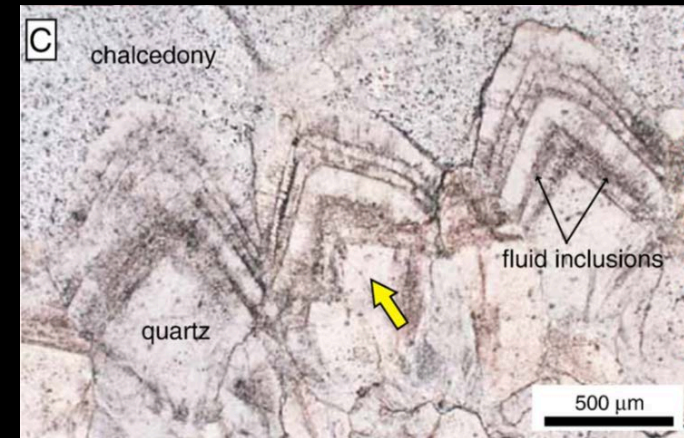
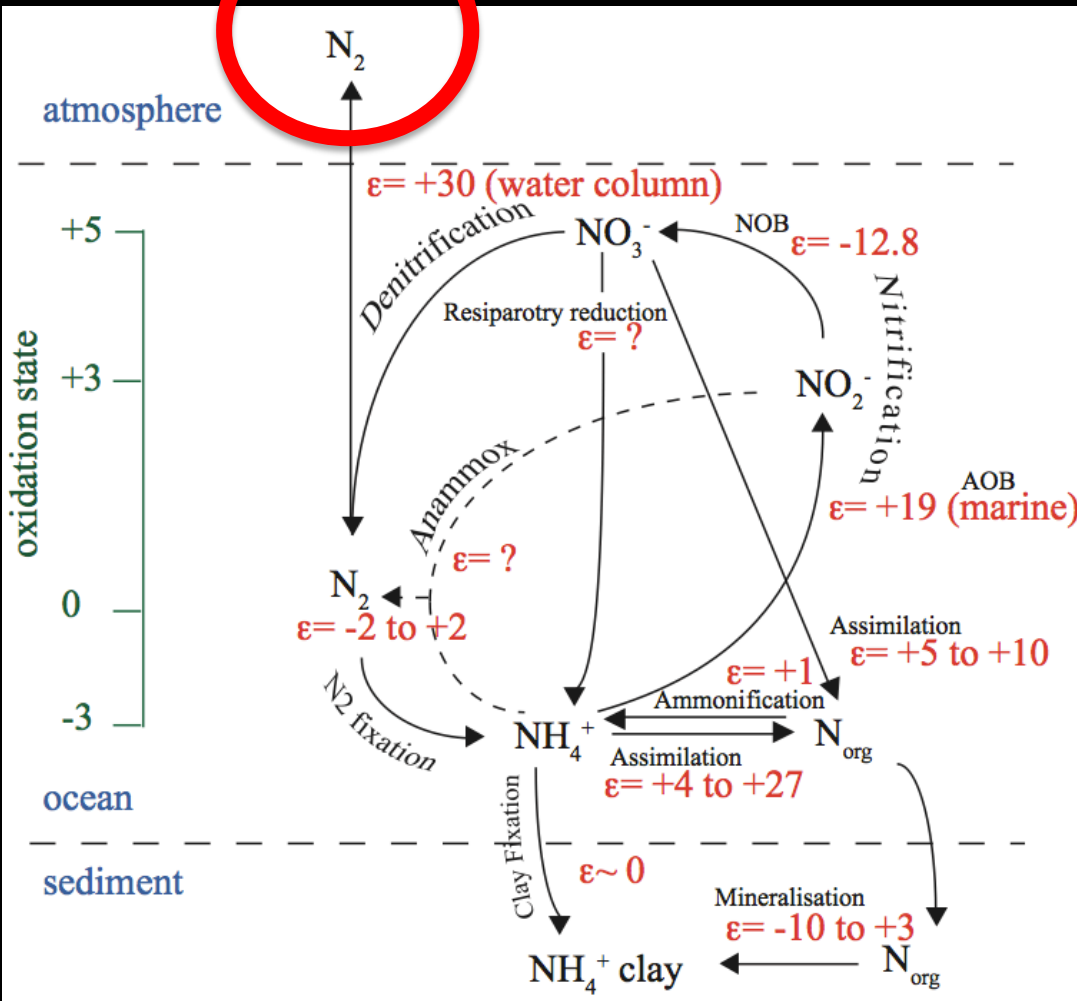
➤ Allow $\delta^{15}\text{N}$ determination with a precision of $\pm 0.5\text{‰}$ (2σ) on ~ 30 nmol of Nitrogen



Early Earth complications

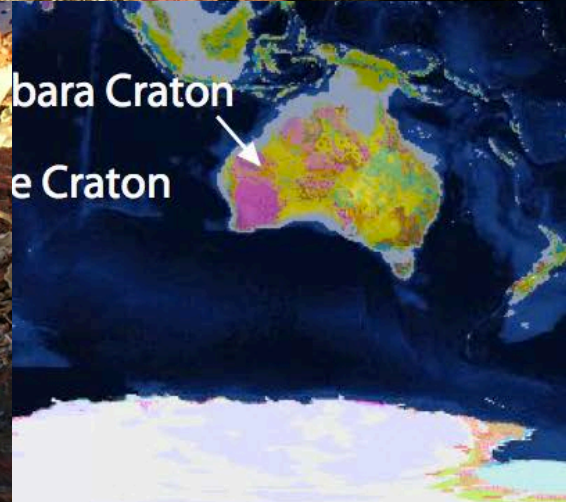
$\delta^{15}\text{N}$ of air ?

- $\delta^{15}\text{N}$ N_2 -bearing fluid inclusion at 3.5 Ga close to 0‰ (*Nishizawa, 2007*)
- N_2 reservoir does not evolve significantly ? (*Marty, 2015*)

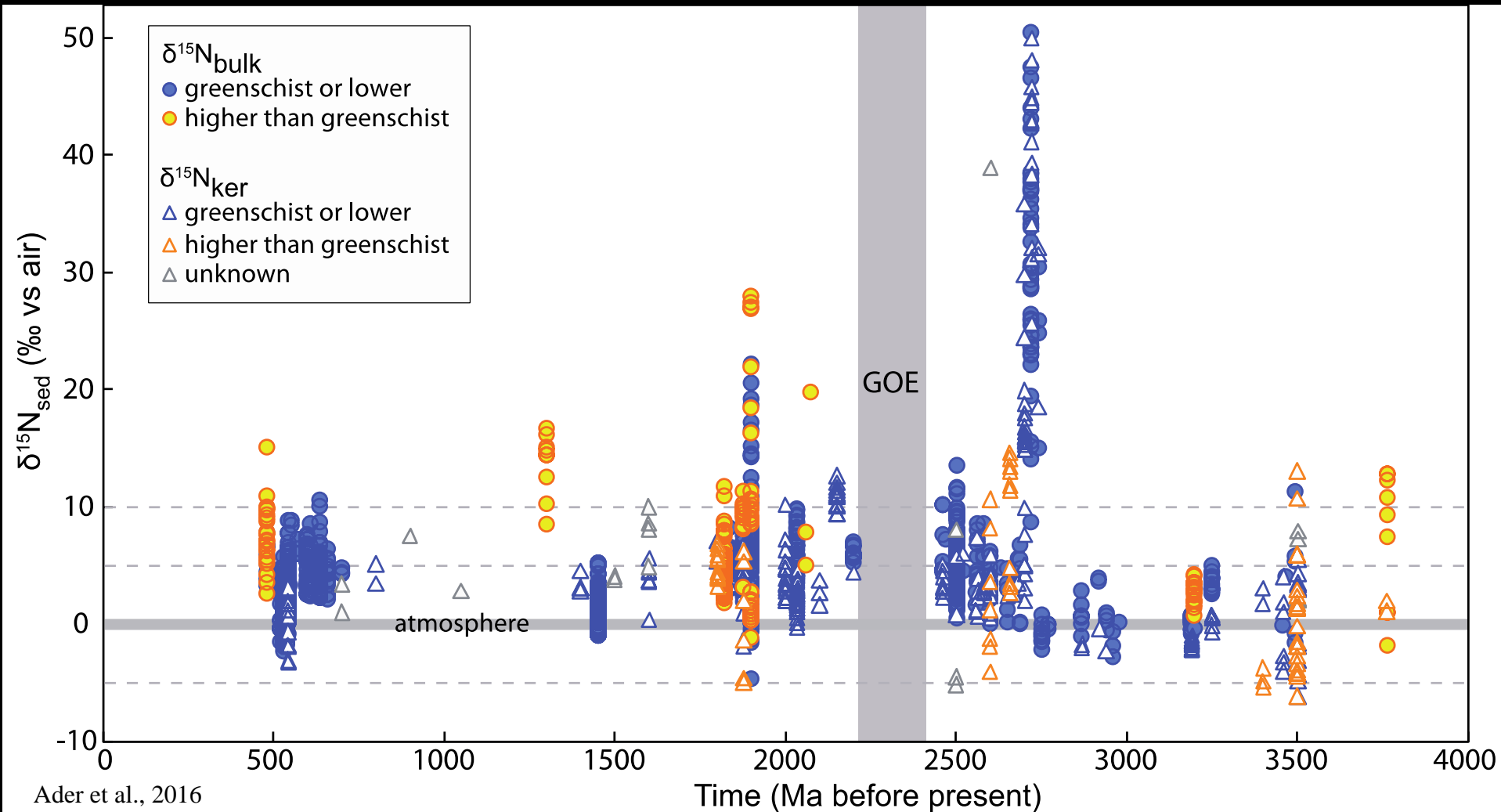


Precambrian sedimentary nitrogen isotopes

➤ Compilation of **874 published** $\delta^{15}\text{N}$ between 3.8 Ga and 500 Ma. Measured on various Precambrian sedimentary lithologies and phases (Kerogen, Phyllosilicates, shales and carbonates, cherts and BIFs and N_2 -bearing fluid inclusion).

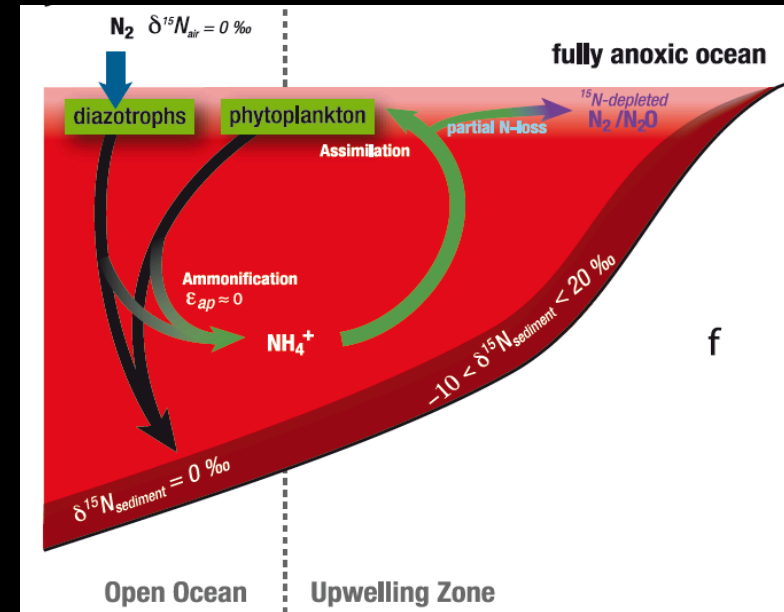
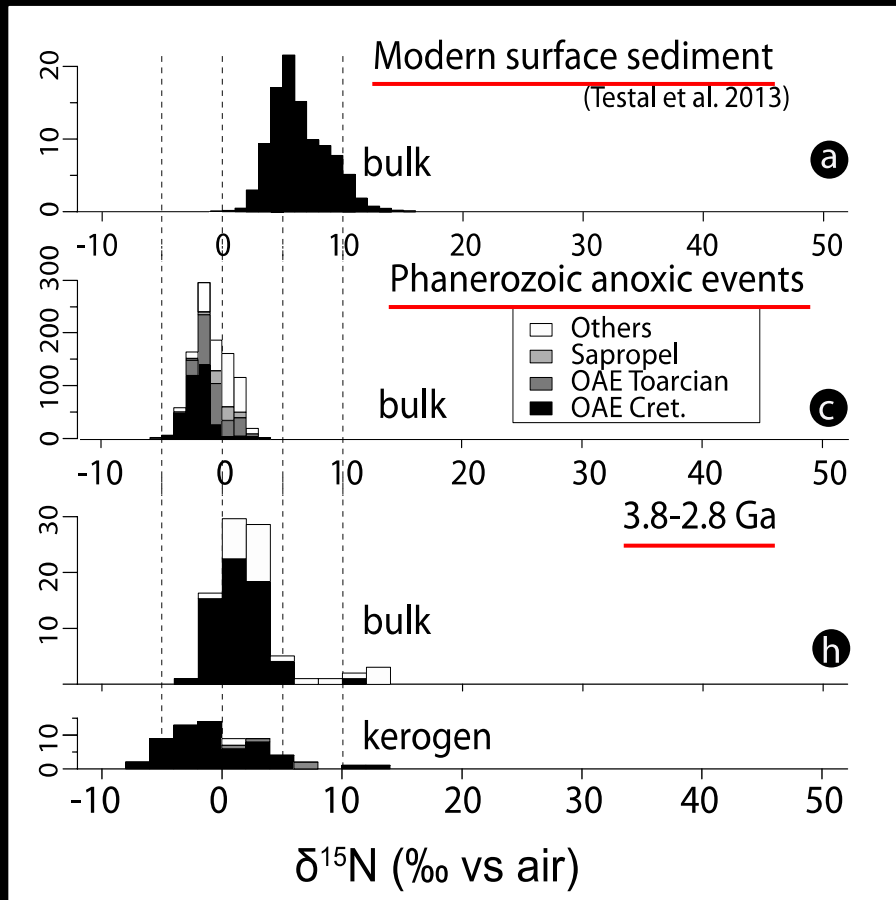


Precambrian sedimentary nitrogen isotopes



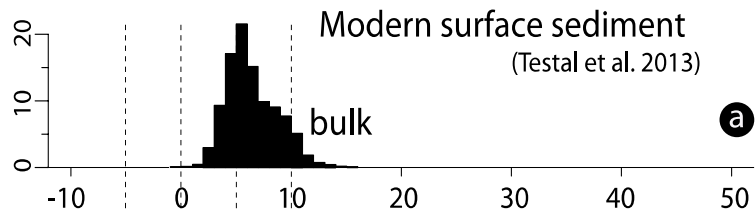
3.8 – 2.8 Ga

$\delta^{15}\text{N}$ mode $\approx 1\%$
 \Rightarrow minor fractionation
 consistent with fully anoxic
 oceans

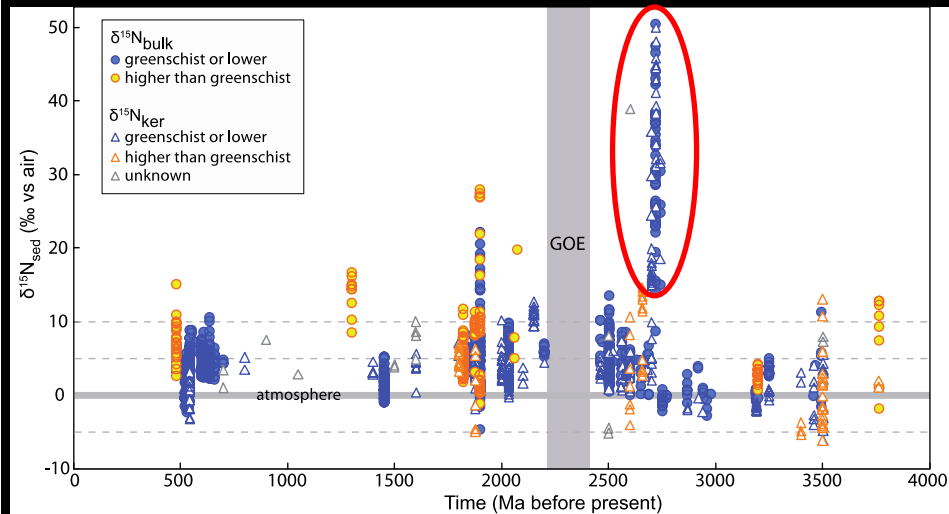
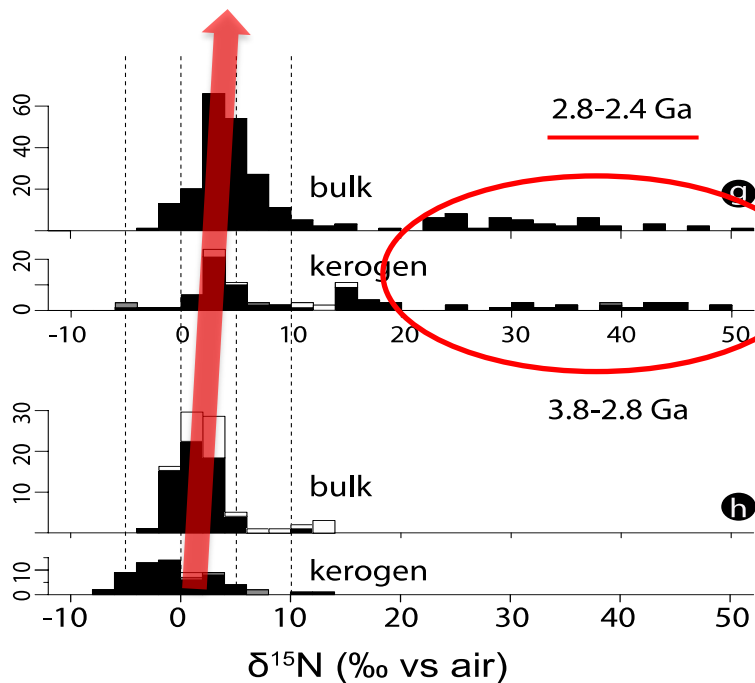


➤ Ammonium is the main
 bioavailable fixed N species

2.8 – GOE

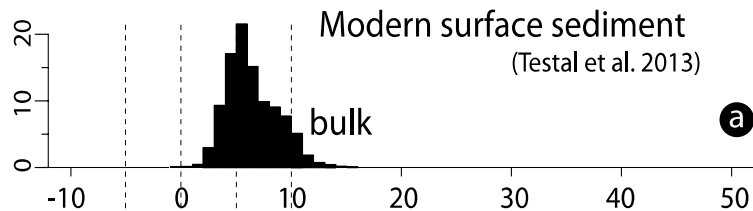


Increase in $\delta^{15}\text{N}$ mode $\approx 3\%$

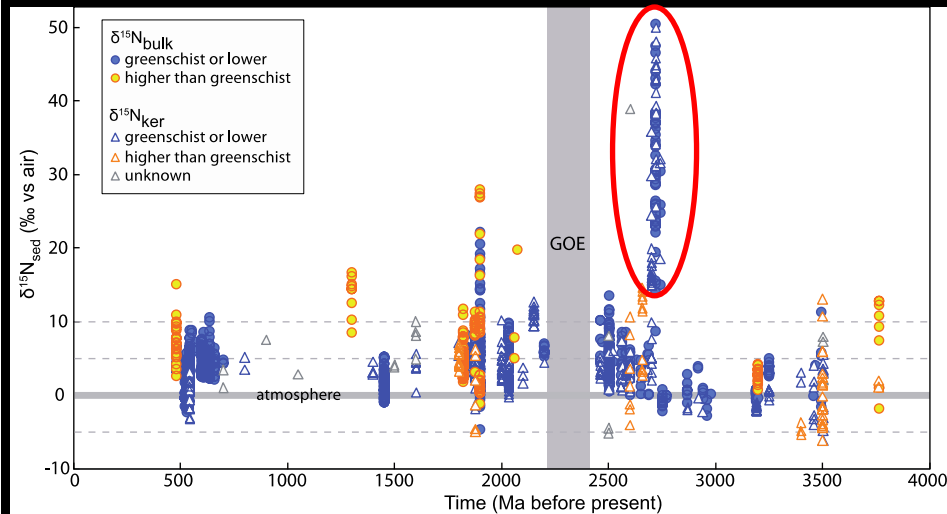
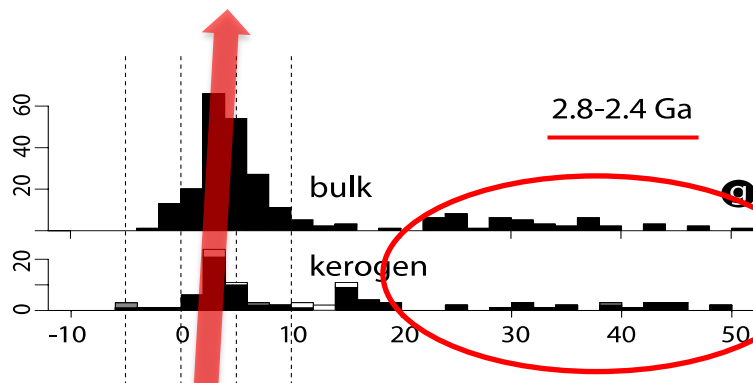


... values up to 55‰ !

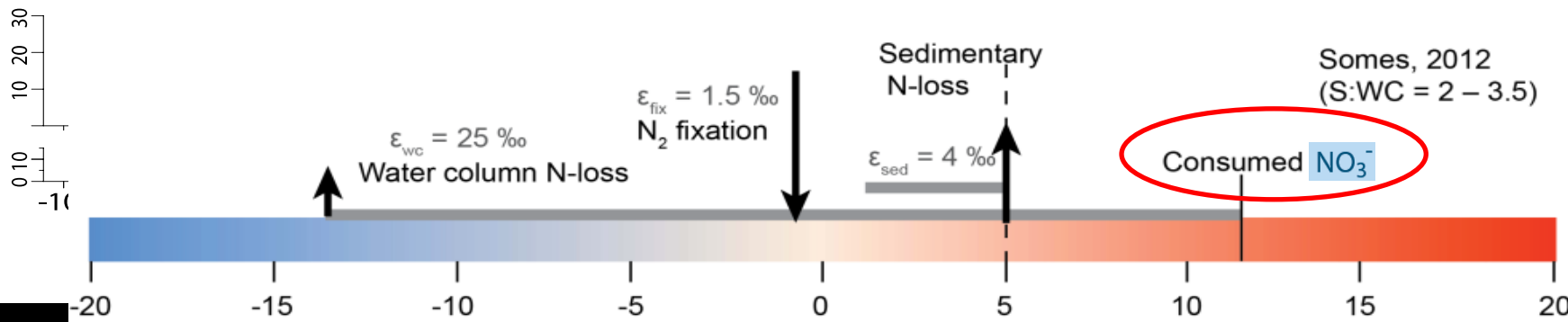
2.8 – GOE



Increase in $\delta^{15}\text{N}$ mode ≈ 3 ‰

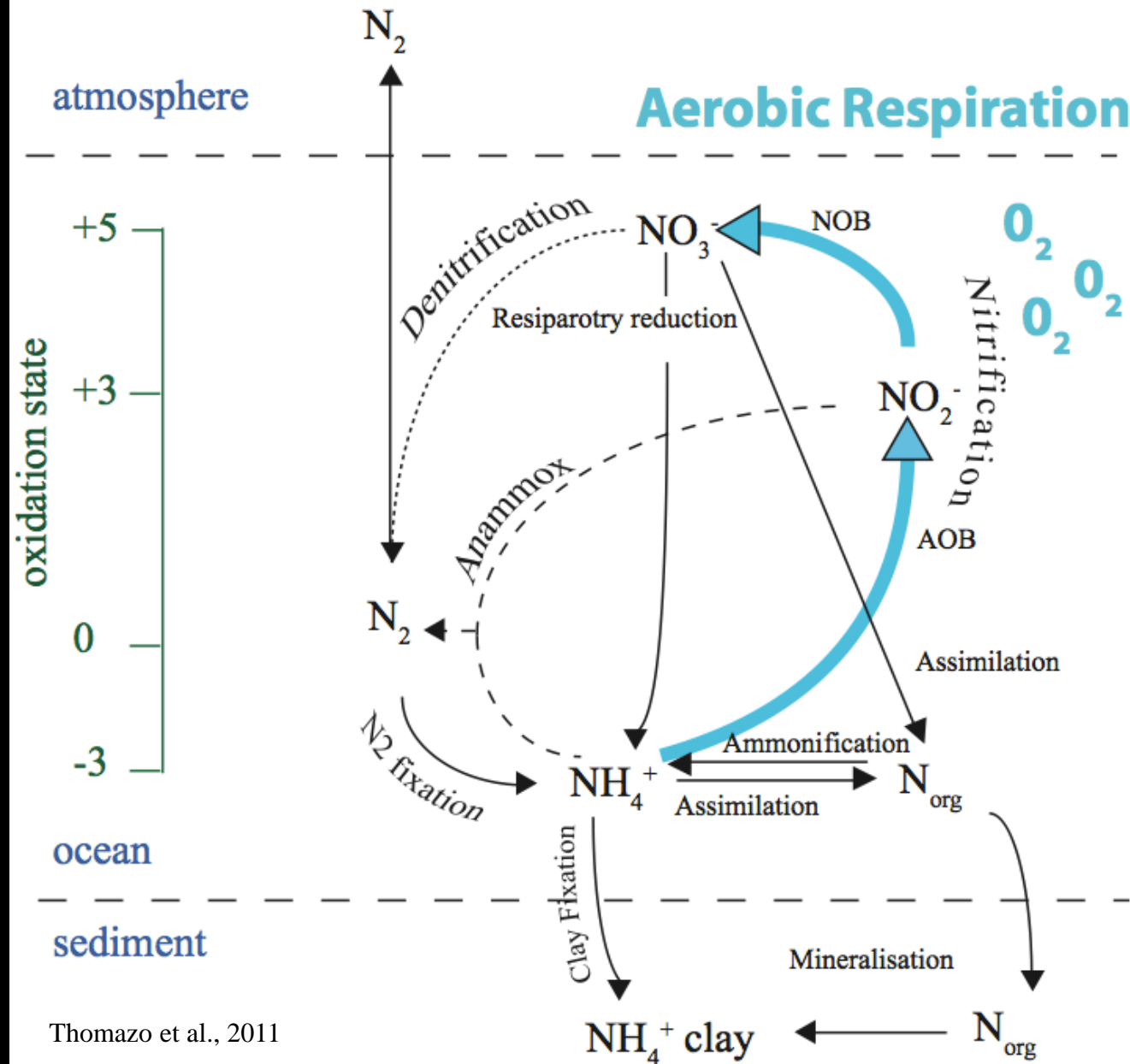


... values up to 55‰ !

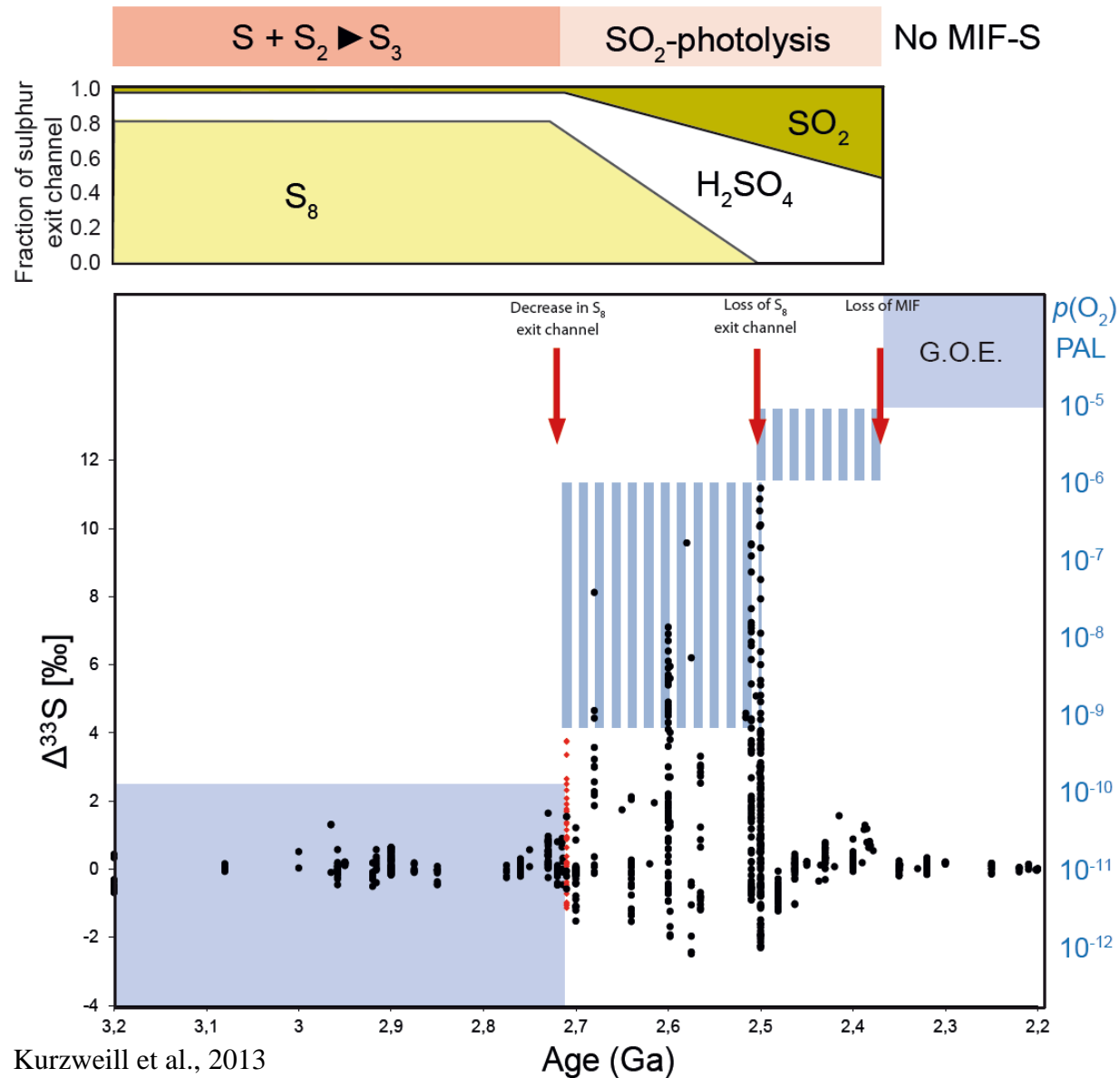


2.8 – GOE

- occurrence of O_2 (possibly cryptic) in Archean oceans
- *Must have help to slowly grow a stable nitrate reservoir (nitrification)*



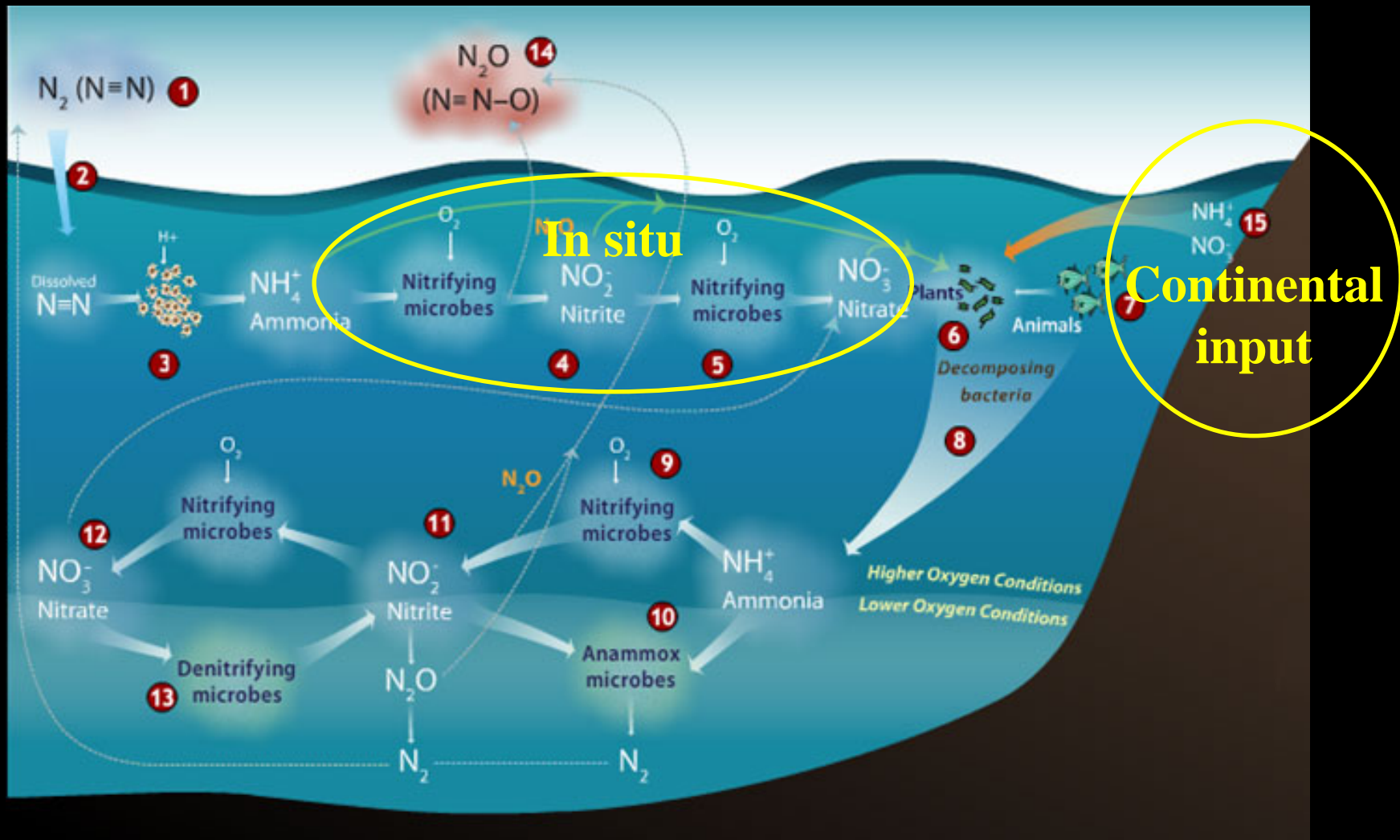
2.8 – GOE



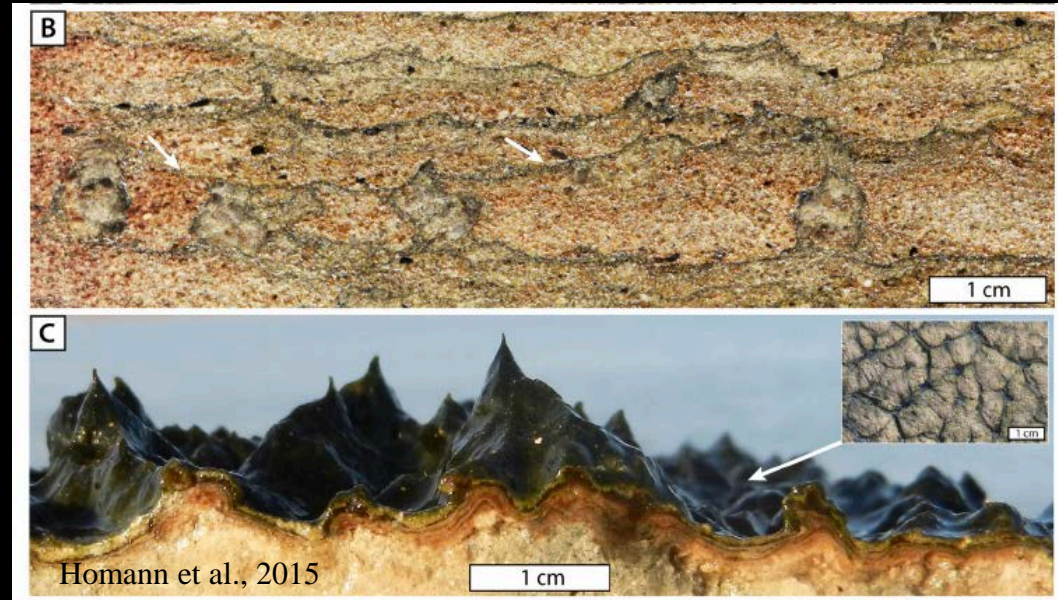
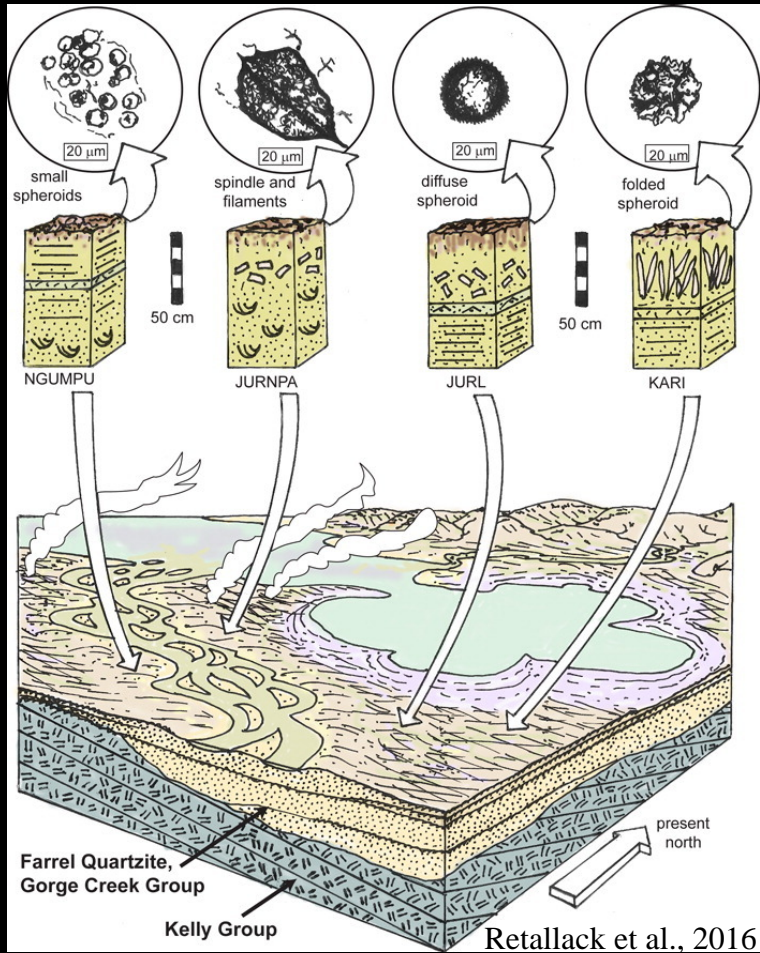
➤ Consistent with MIFs record (increase in oxygen!)

Lessons from the modern N cycle

Origin of the nitrate signal preserved in the $\delta^{15}\text{N}$ sedimentary record?



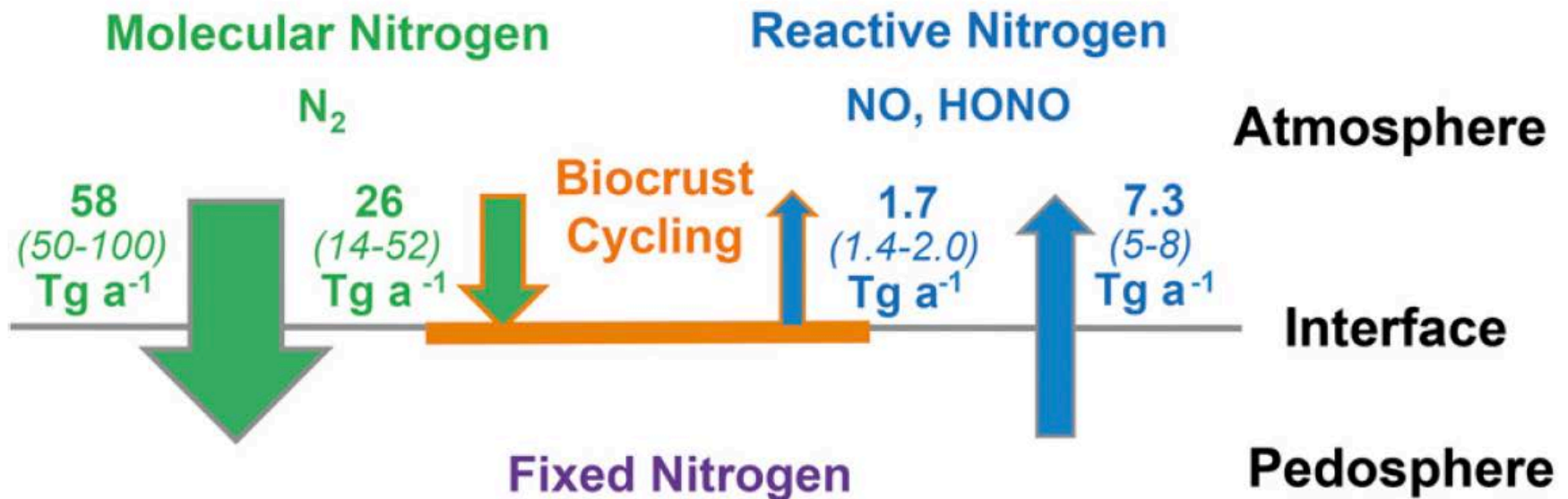
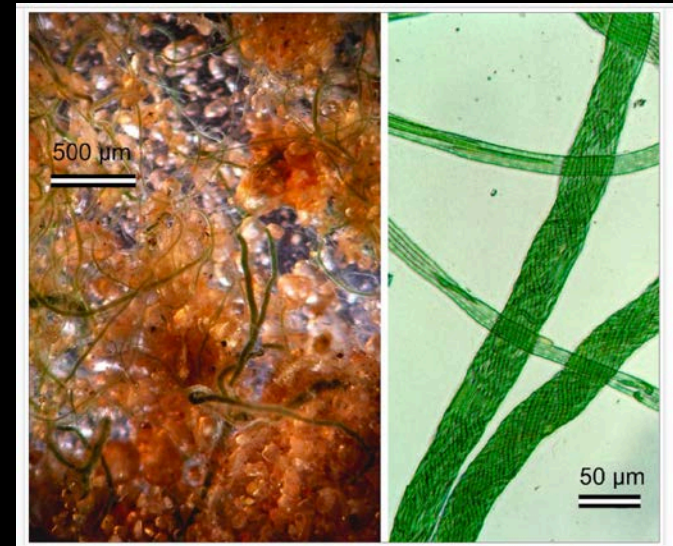
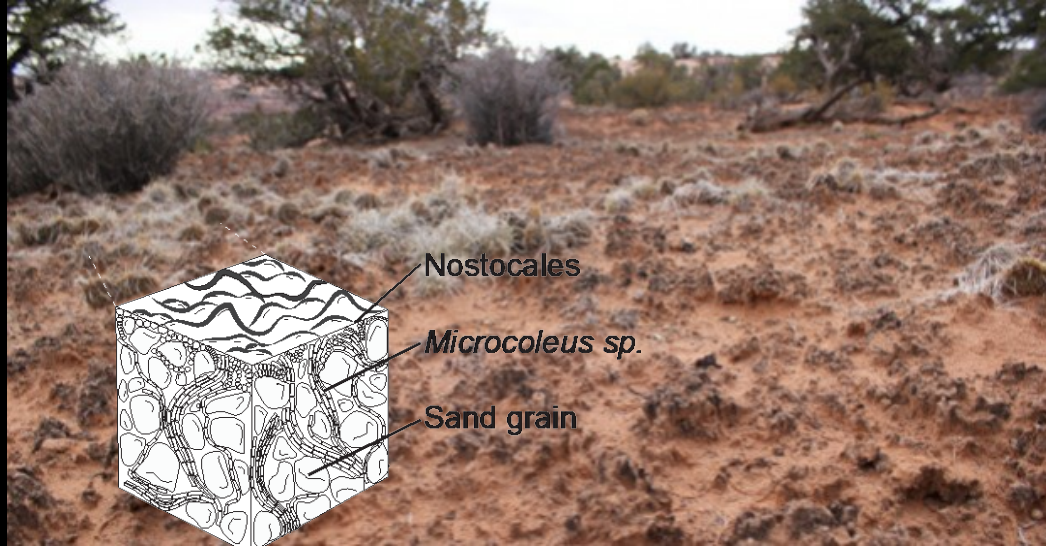
An Archean continental biomass ?



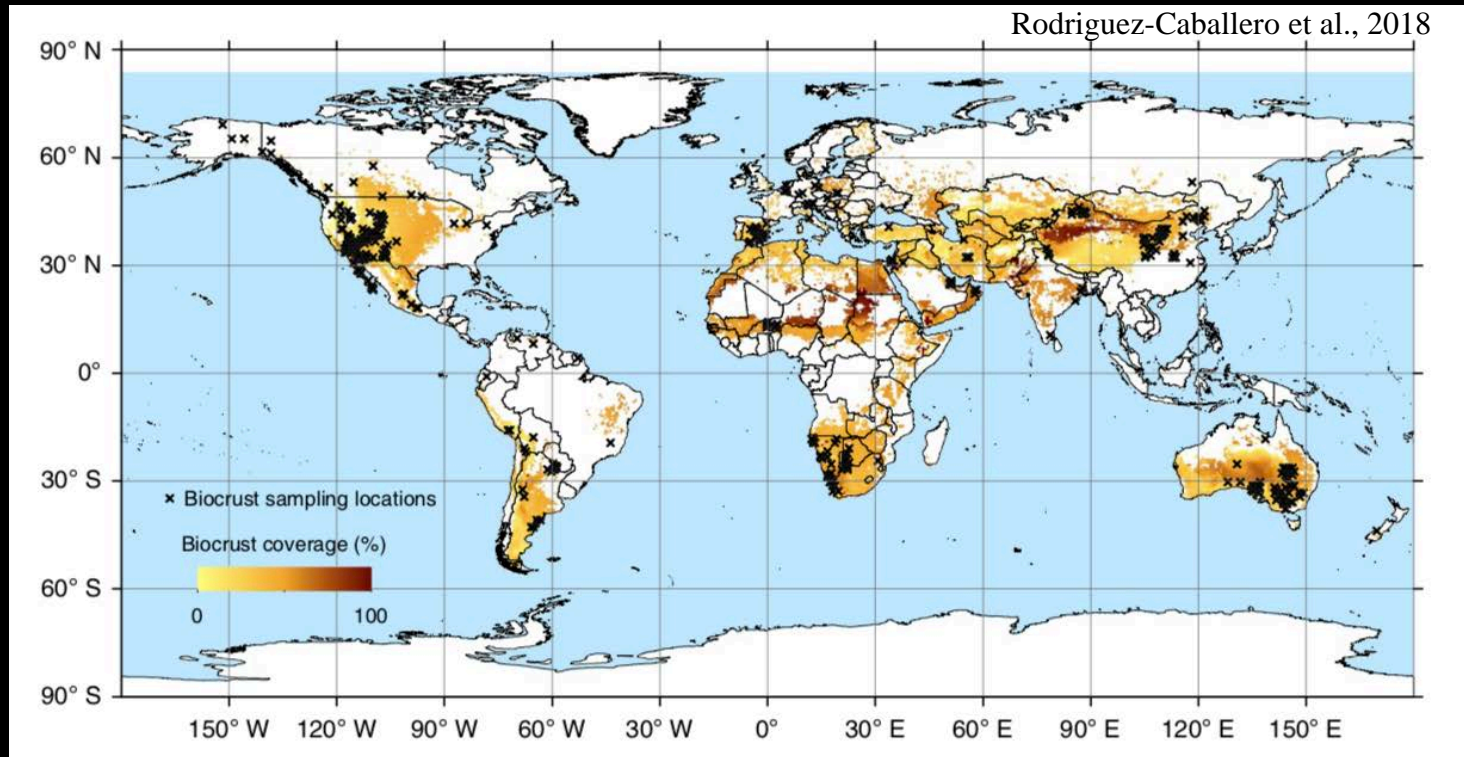
Wavy-crinkly microbial mats - 3.2 Ga Moodies Group sandstone (South Africa)

Coastal-plain paleosols - 3.0 Ga
Farrel Quartzite (Western Australia)

Modern Biocrusts



Modern Biocrusts

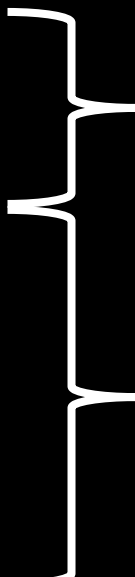


- Modern BSCs are arguably the most extensive biofilm on the planet covering up to 12% of Earth's continental area
- They are primarily built by cyanobacteria performing oxygenic photosynthesis

Modern Biocrusts

Modern Biocrusts

	Location	Net N outputs from crusts to subsurface soil ($\text{m}^{-2} \text{yr}^{-1}$)
Johnson et al. ⁴³	Colorado Plateau	2.080–8.820 ^a
Thiet et al. ⁴⁶	Lake Michigan	0.020–0.800 ^a
Rychert & Skujins ⁴⁹ ; West & Skujins ⁵⁰	Cold desert	0.19–1.9
Rychert et al. ⁵¹	Australia	0.025
Evans & Johansen ⁵²	Sonoran Desert	0.133–0.342
Evans & Lange ⁵³ ; Belnap ^{54, 55} ; Russow et al. ⁵⁶ ; Stewart et al. ^{57, 58, 59} ; Caputa et al. ⁶⁰	Global	0.0133–1.9
Elbert et al. ⁴²	Global	0.144 ^b


 Direct estimate
 extrapolated from the nitrogen import fluxes
 = *N input times 19% of export*

Modern Biocrusts

	Location	Net N outputs from crusts to subsurface soil ($\text{m}^{-2} \text{yr}^{-1}$)
Johnson et al. ⁴³	Colorado Plateau	2.080–8.820 ^a
Thiet et al. ⁴⁶	Lake Michigan	0.020–0.800 ^a
Rychert & Skujins ⁴⁴		
Rychert et al. ⁵¹		
Evans & Johansen		
Evans & Lange ⁵³ ; E Stewart et al. ^{57,58}		
Elbert et al. ⁴²		

} Direct estimate

Handwritten notes on lined paper:

N transport to underlying soil (from literature)

conversion to T_g

surface contour

conversion to m^2

$$F(\text{g} \cdot \text{m}^{-2} \cdot \text{y}^{-1}) \times 10^{-12} \times S(\text{km}^2) \times 10^6 = F_{(s)}(\text{Tmol} \cdot \text{y}^{-1})$$

$M(\text{g} \cdot \text{mol}^{-1})$

$N_{\text{mesoindicate}}$

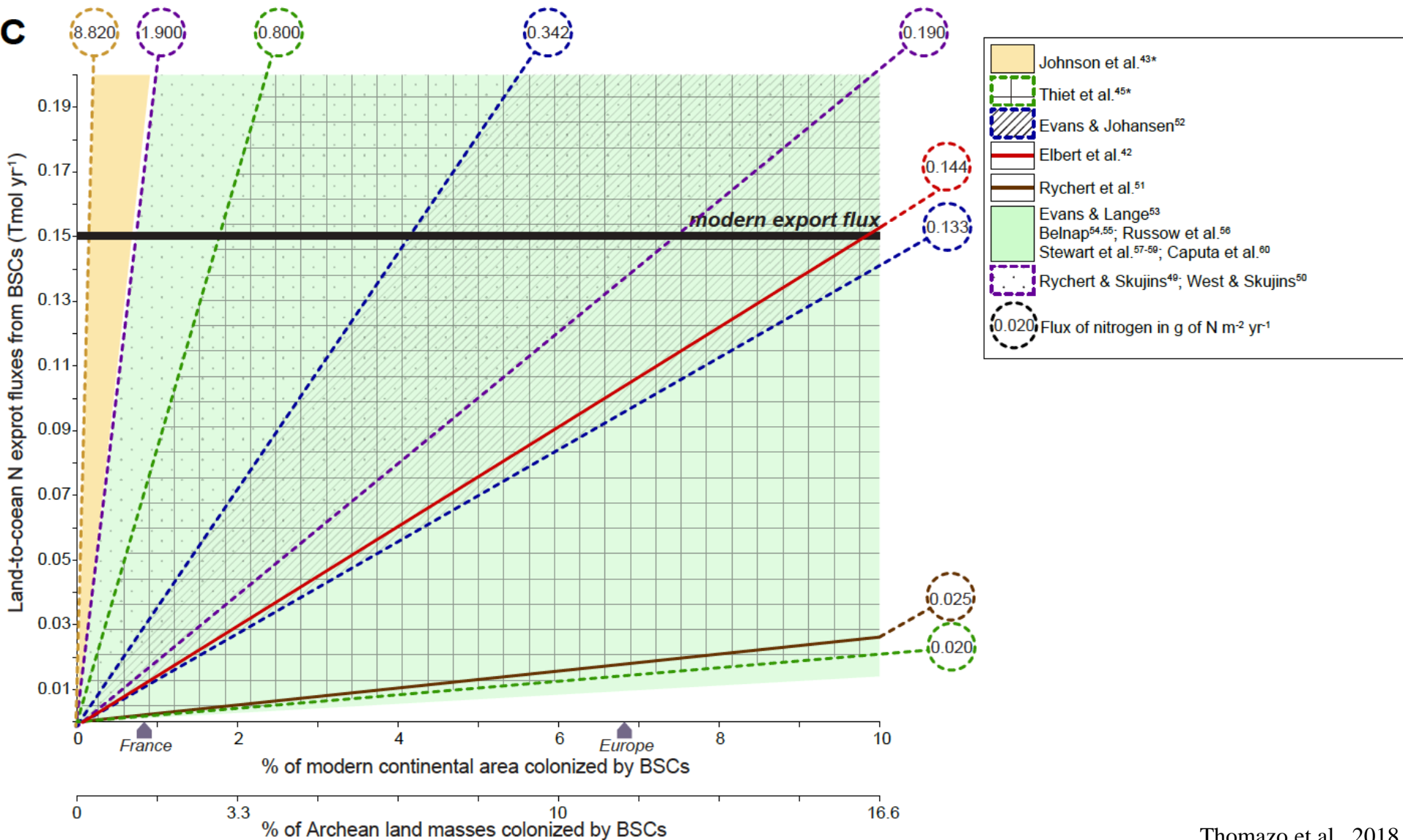
Total exported N in Tmol/year for a given (flux) and surface(s)

plots $\rightarrow F$ (sheet 1)

Sheet 3

and from
import

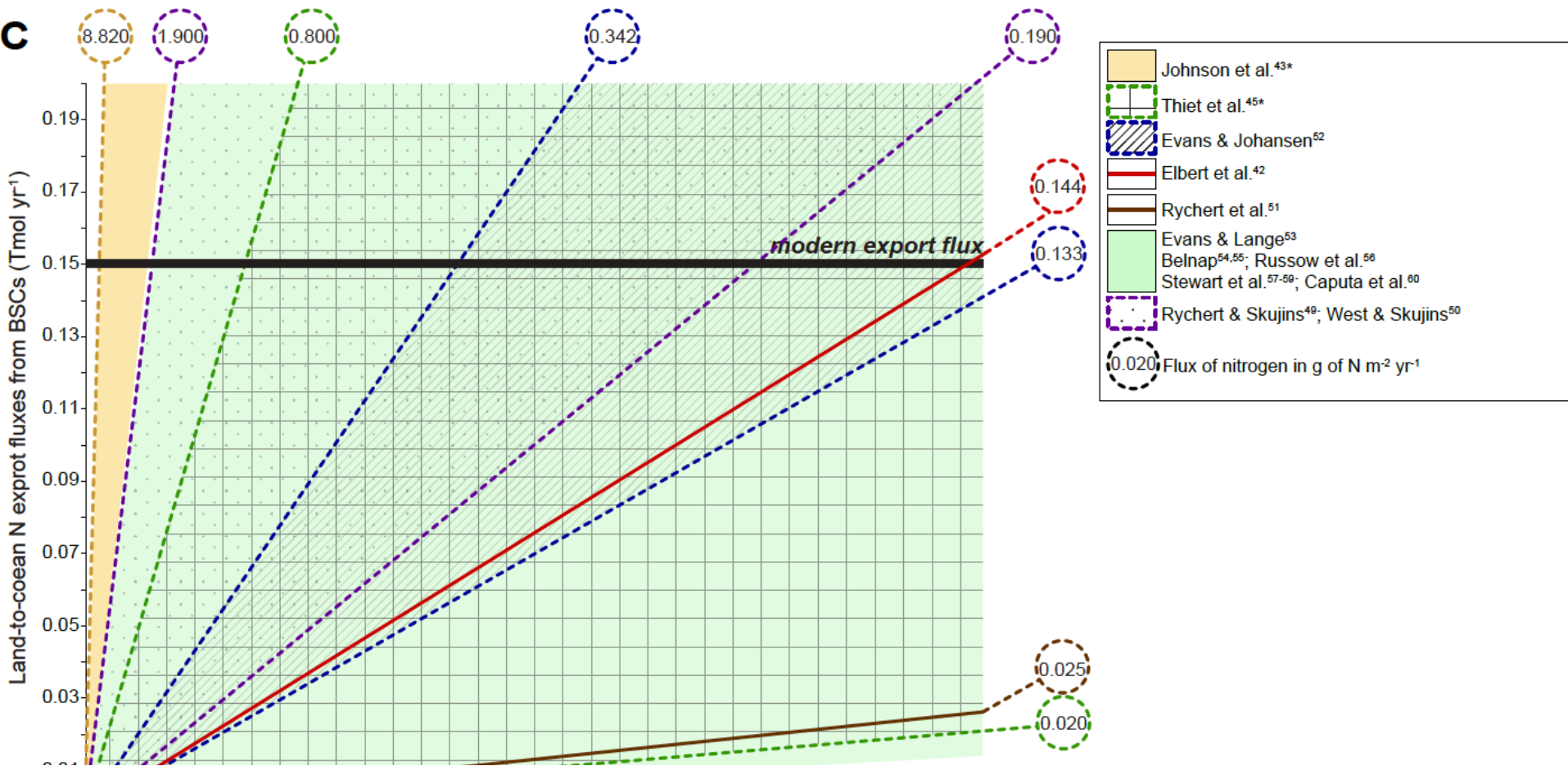
Modern Biocrusts



Thomazo et al., 2018

assuming a total emerged surface of about 90 Mkm² at around 2.45 Ga, i.e., 60% of the present day value

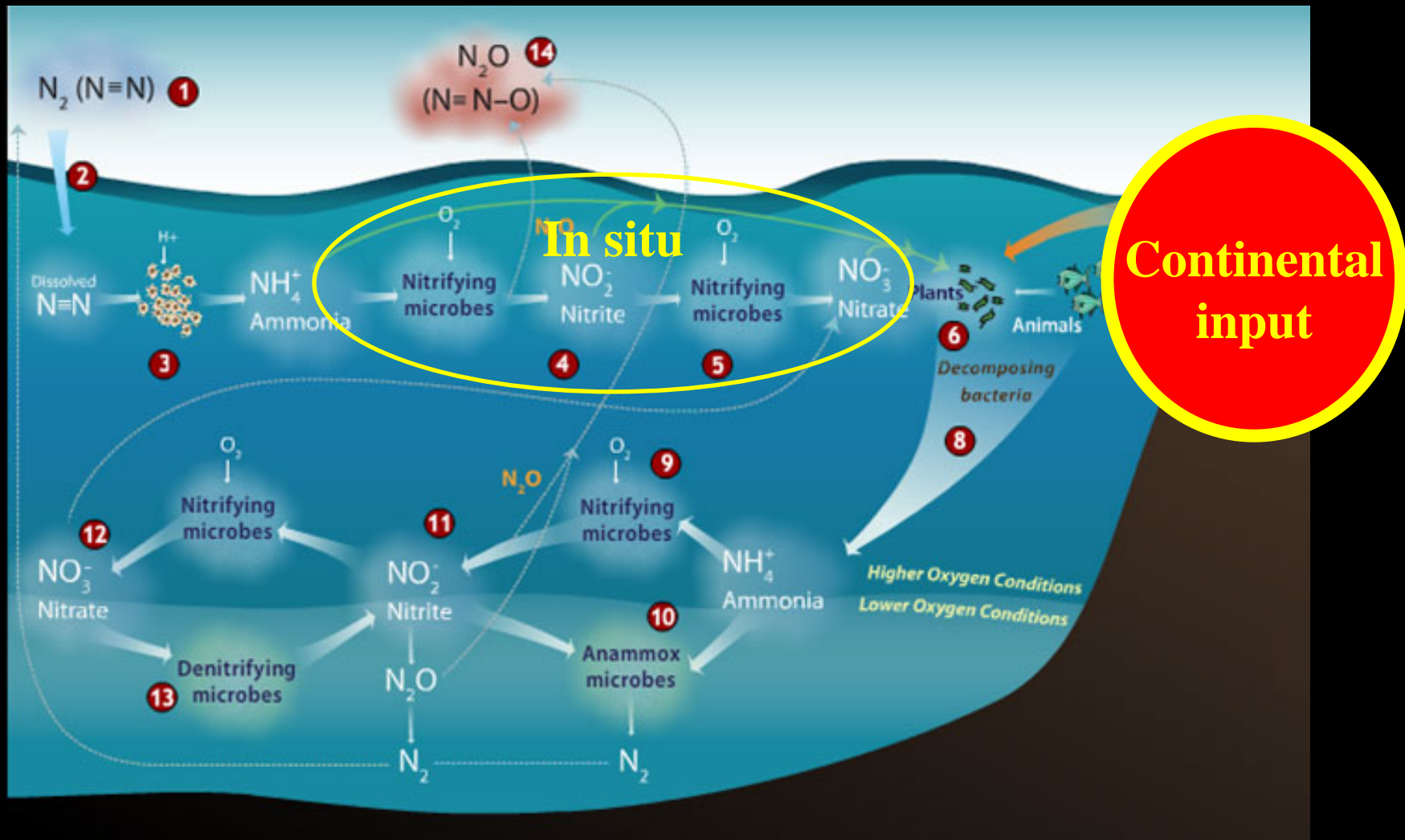
Modern Biocrusts



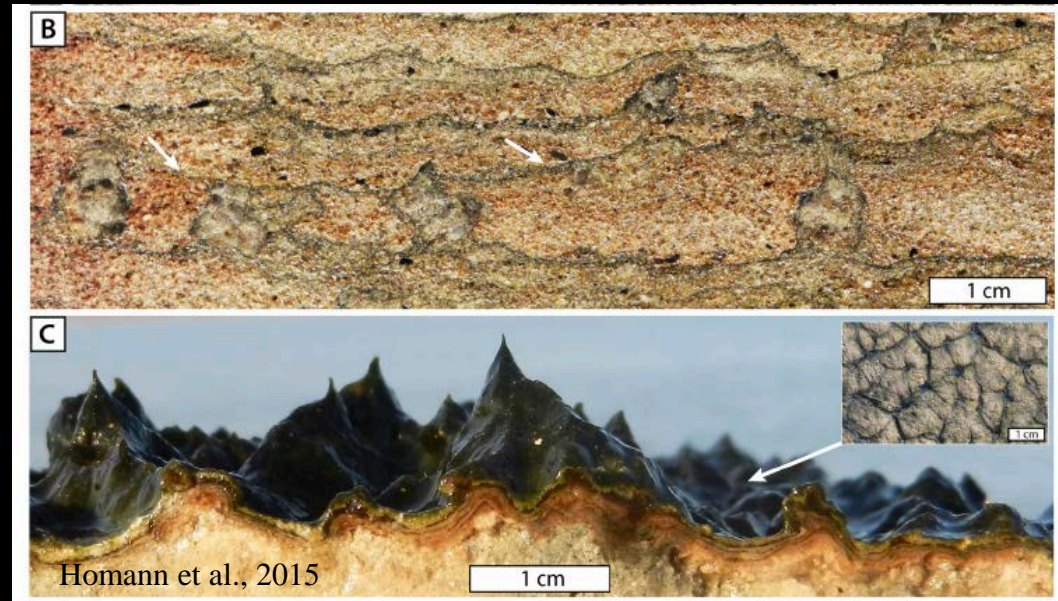
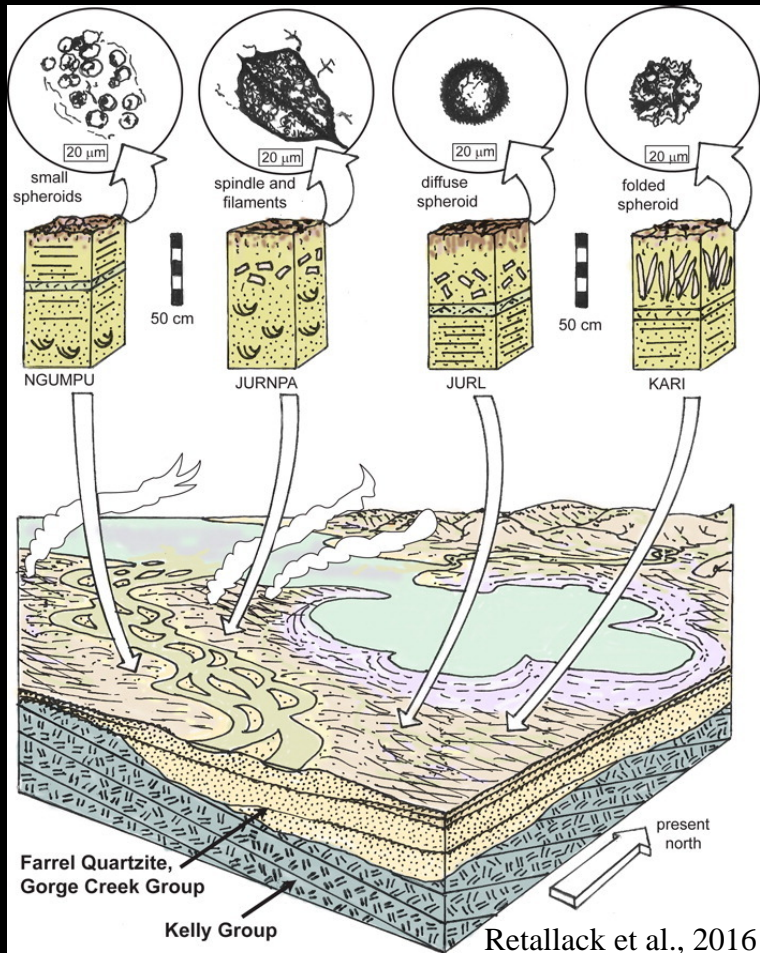
Large range of fluxes but averages direct and indirect estimates suggest that between 16% of colonization of Archean continents with terrestrial « cyanobacteria » would be enough to recapitulate the modern N export from land to ocean!

Lessons from the modern N cycle

Origin of the nitrate signal preserved in the $\delta^{15}\text{N}$ sedimentary record?



Archean record of Biocrusts?



Wavy-crinkly microbial mats - 3.2 Ga Moodies Group sandstone (South Africa)

Coastal-plain paleosols - 3.0 Ga
Farrel Quartzite (Western Australia)

Archean record of Biocrusts?

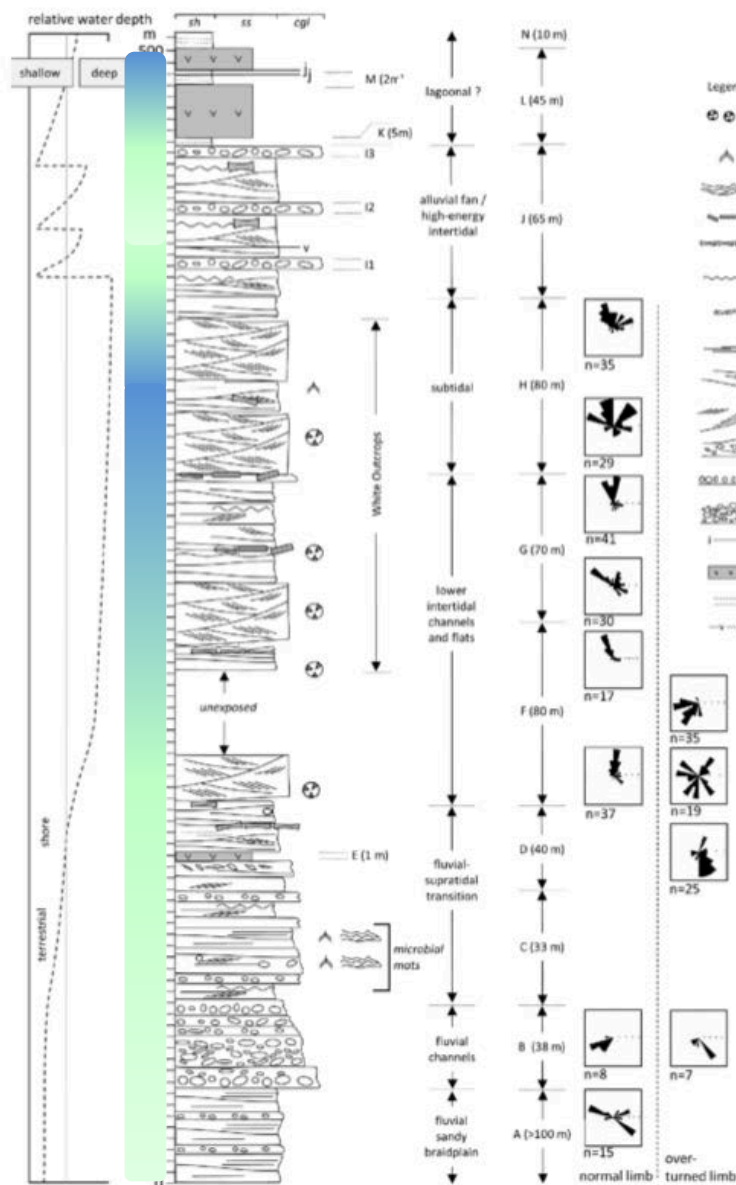
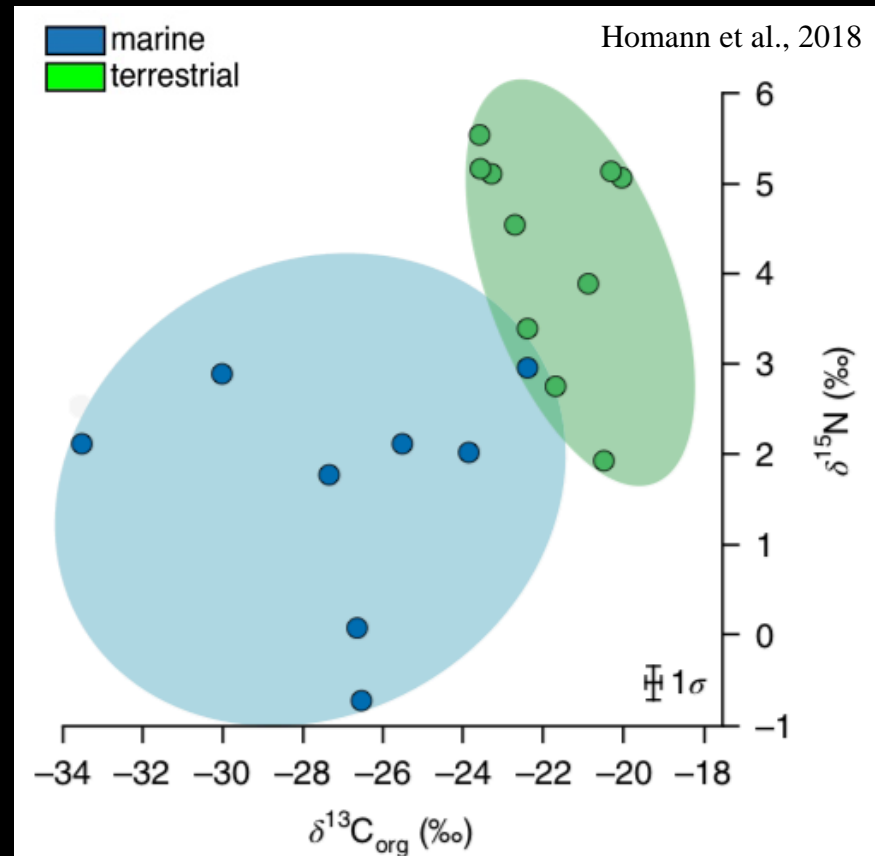
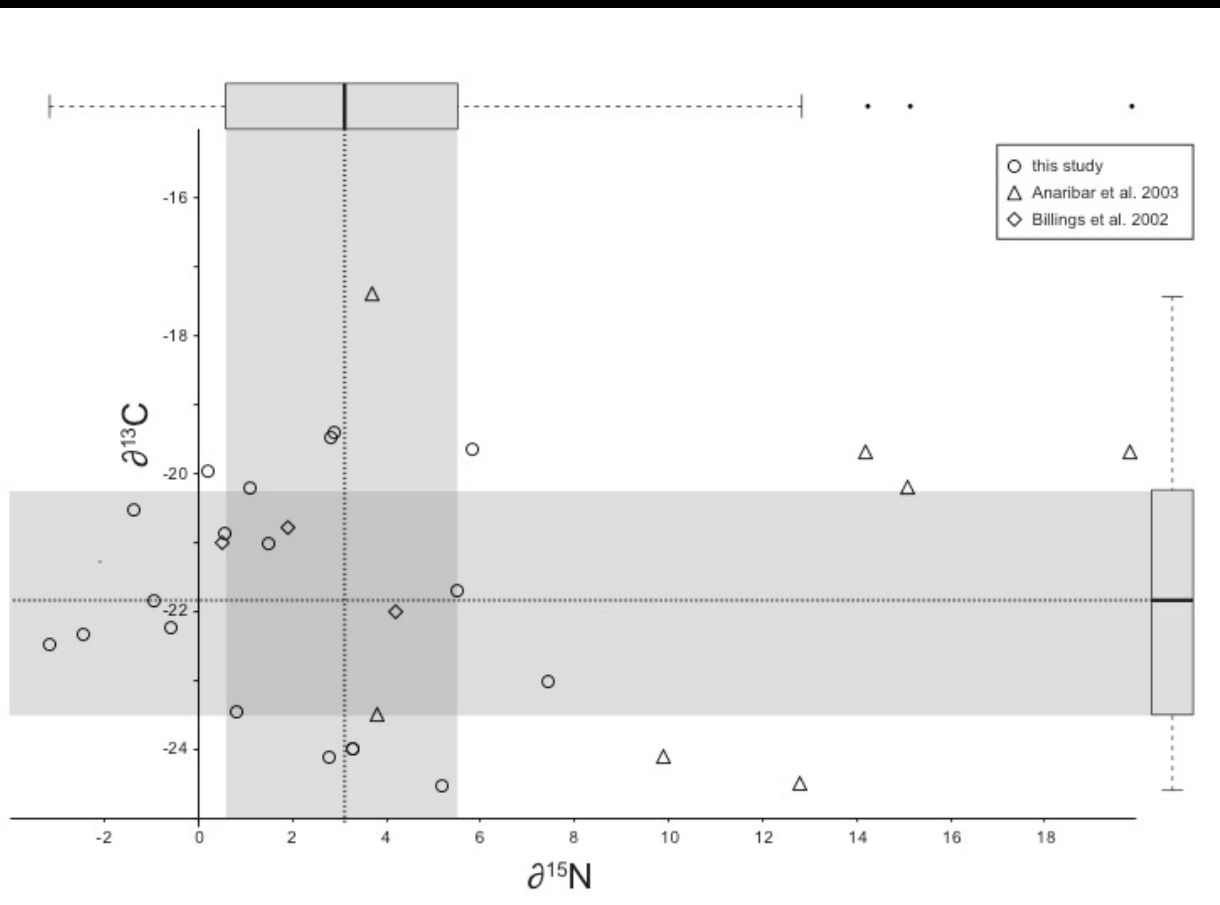


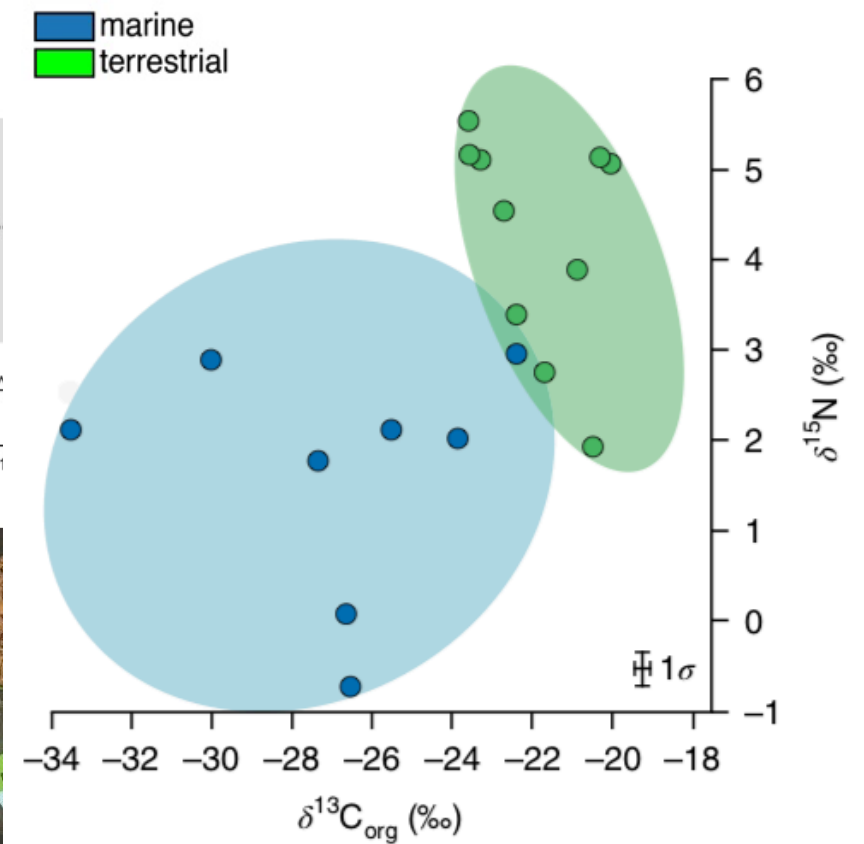
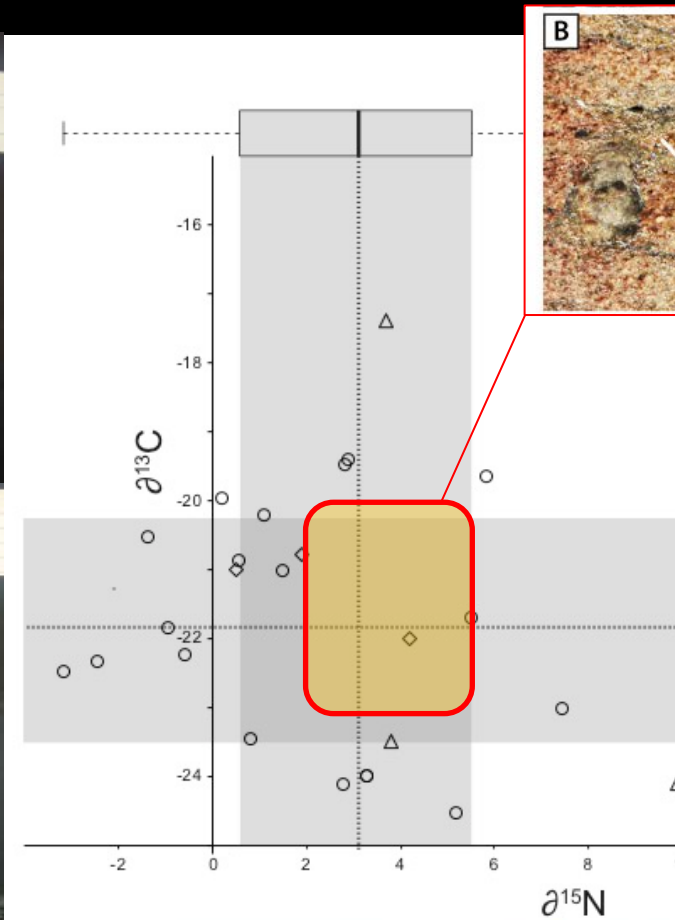
Figure 5. Stratigraphic column of Moodies stromatolite structures in the western Dwyka Group, measured along the normal limb.



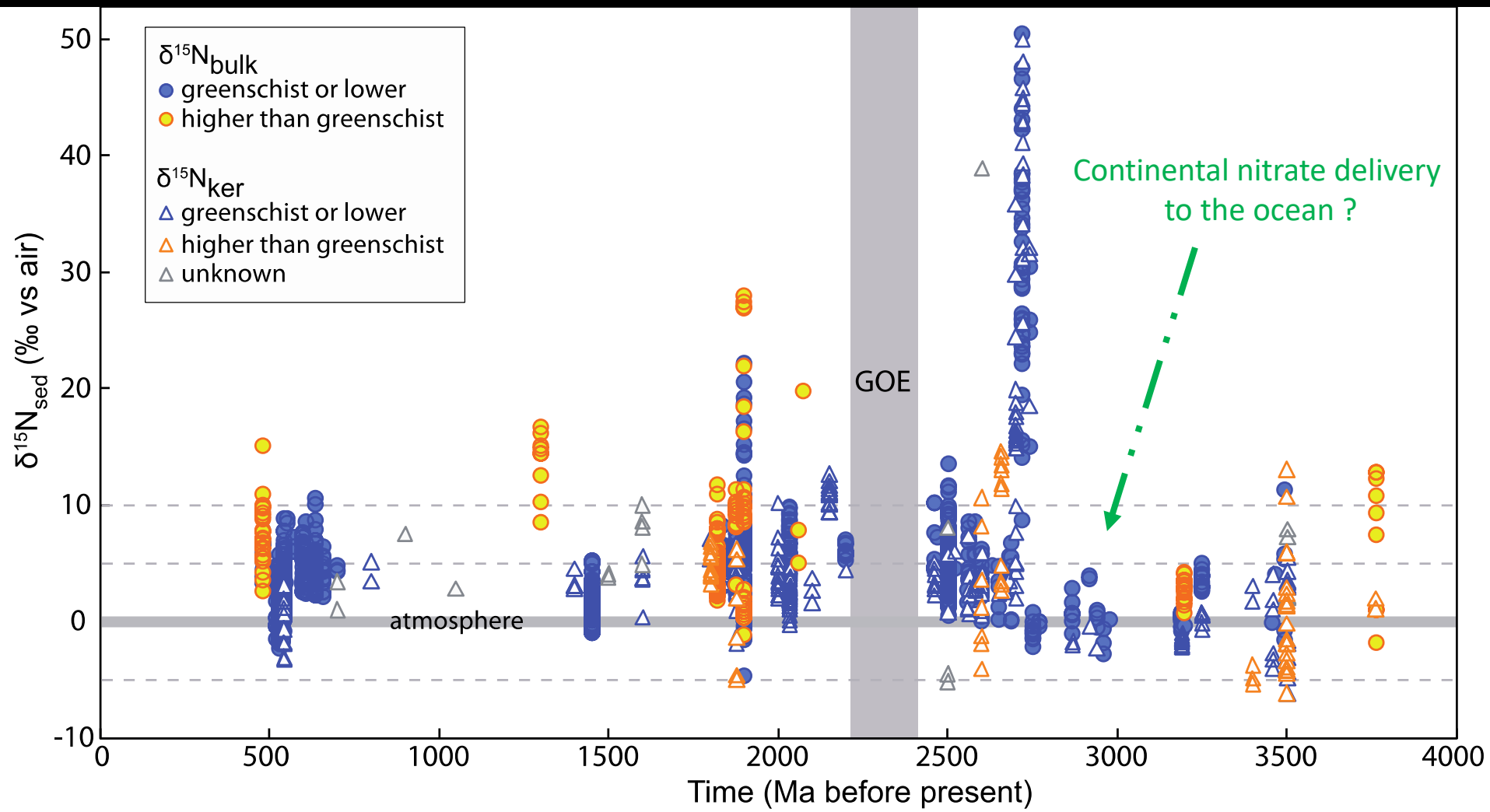
Archean record of Biocrusts?



Archean record of Biocrusts?

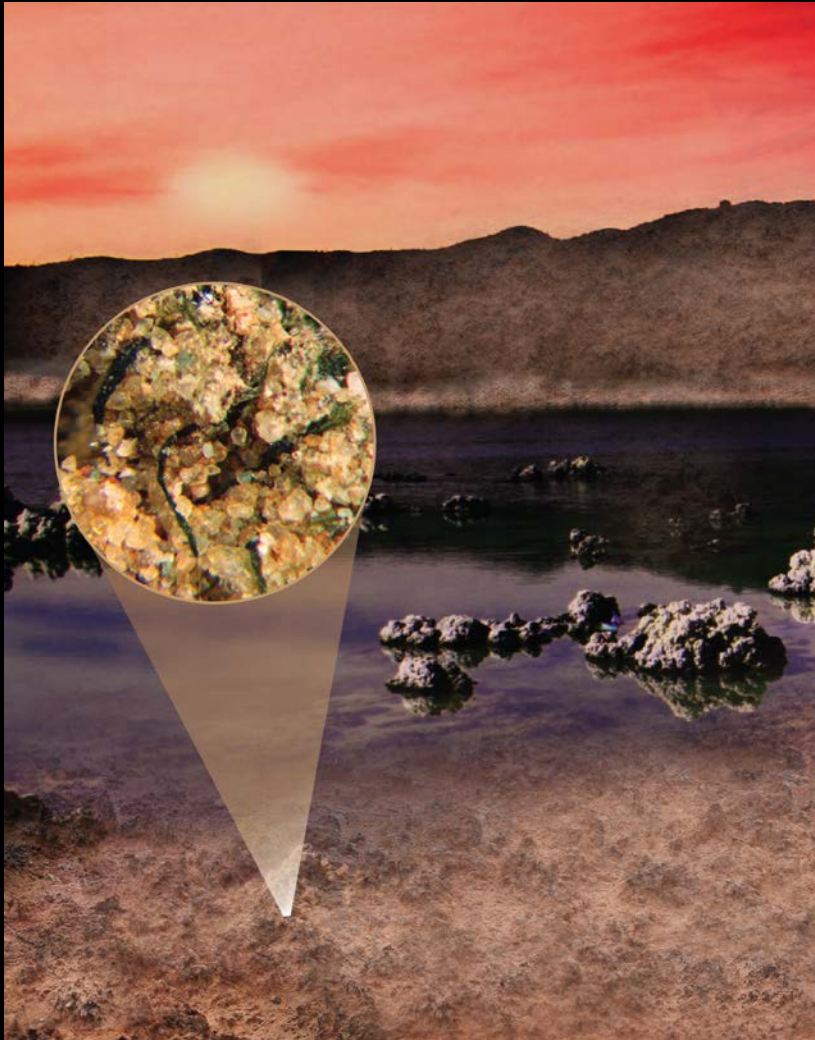


Precambrian sedimentary nitrogen isotopes



Conclusions

- Part of the evolution of the early biogeochemical cycle of nitrogen underline the **increasing oxygen concentration** before the GOE.





- **Nitrate** – the oxidized form of nitrogen – is **cycled by organisms** since at least **2.7 Ga** ($\delta^{15}\text{N}$ record)
- Part of this nitrate may come from a **continental biocrusts-like Archean biosphere** (3.2 Ga – earlier?)

ARTICLE

DOI: 10.1038/s41467-018-04995-y

OPEN

Possible nitrogen fertilization of the early Earth Ocean by microbial continental ecosystems

Christophe Thomazo ¹, Estelle Couradeau ^{1,2} & Ferran Garcia-Pichel²



