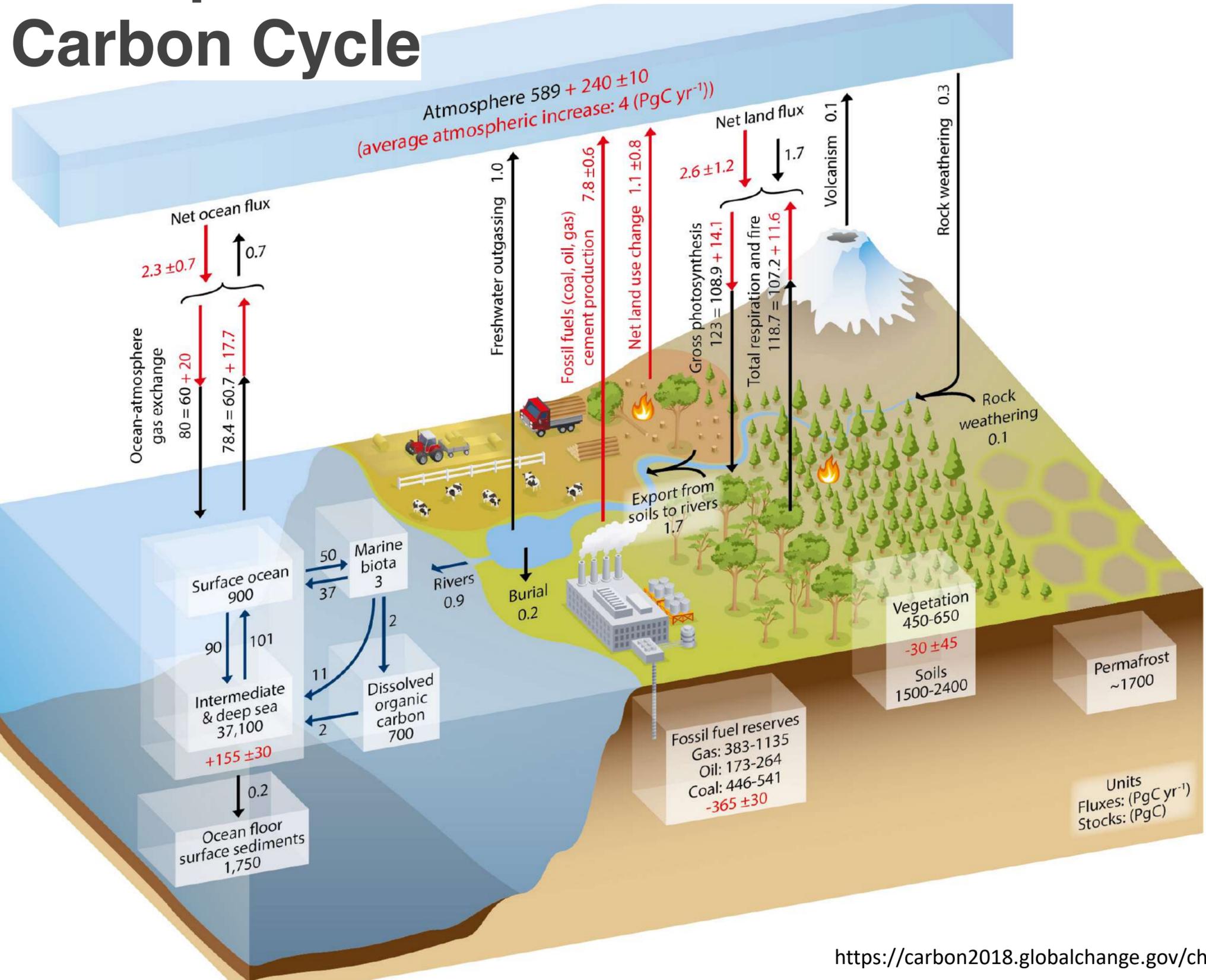


**L04c:**

**Biogeochemical cycle of the  
*other* nutrients (Fe, N, S, P, Si) in  
the ocean**

# A Simplified Pictorial Illustration of the Global Carbon Cycle



The boxed numbers represent reservoir mass or carbon stocks in petagrams of carbon (Pg C, 10<sup>15</sup> grams)

Arrows represent annual exchange (fluxes) in Pg C per year

**Black numbers and arrows represent preindustrial reservoir masses and fluxes,**

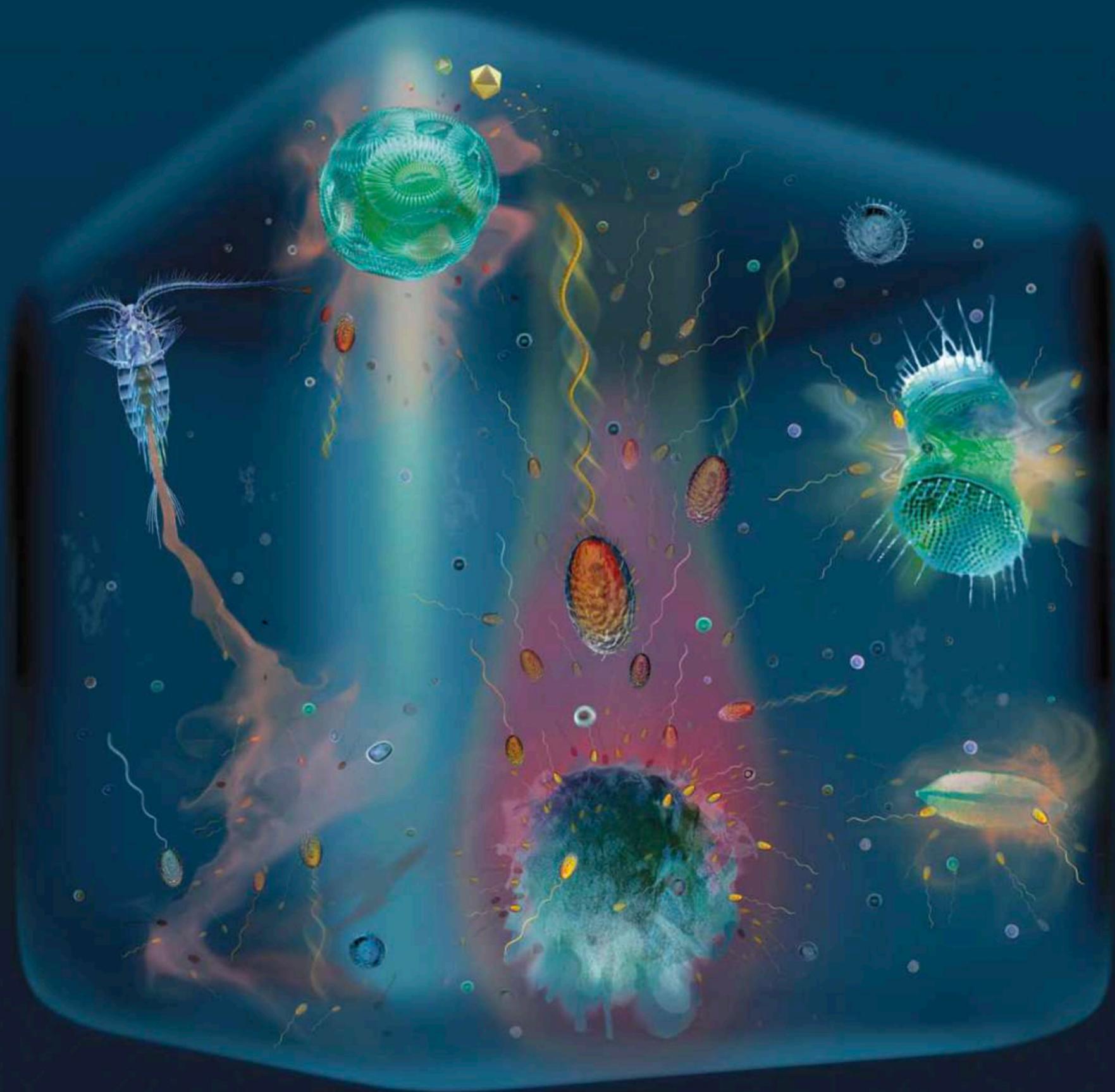
**Red arrows and numbers show average annual anthropogenic fluxes for 2000 to 2009**

**The red numbers in the reservoirs denote cumulative changes of anthropogenic carbon for the industrial period**

**Uncertainties are reported as 90% confidence intervals**

Reprinted from Ciais et al., 2013, Copyright IPCC, used with permission

# Microscale dynamics

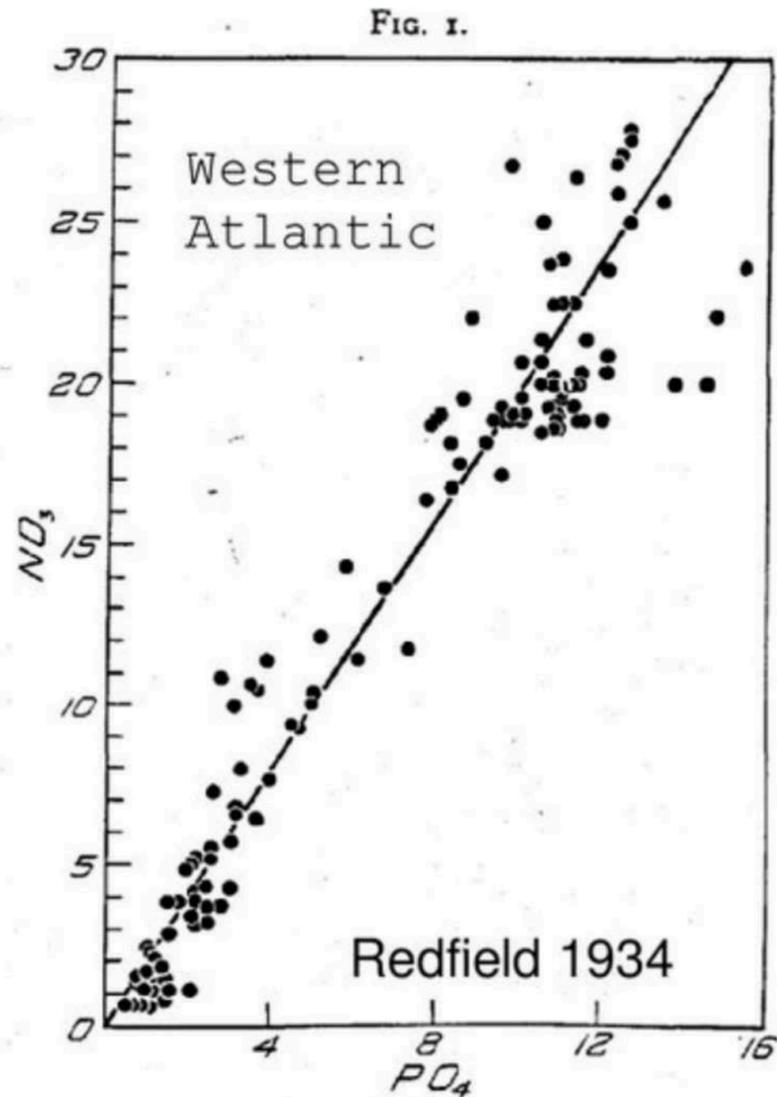


Stocker, 2012

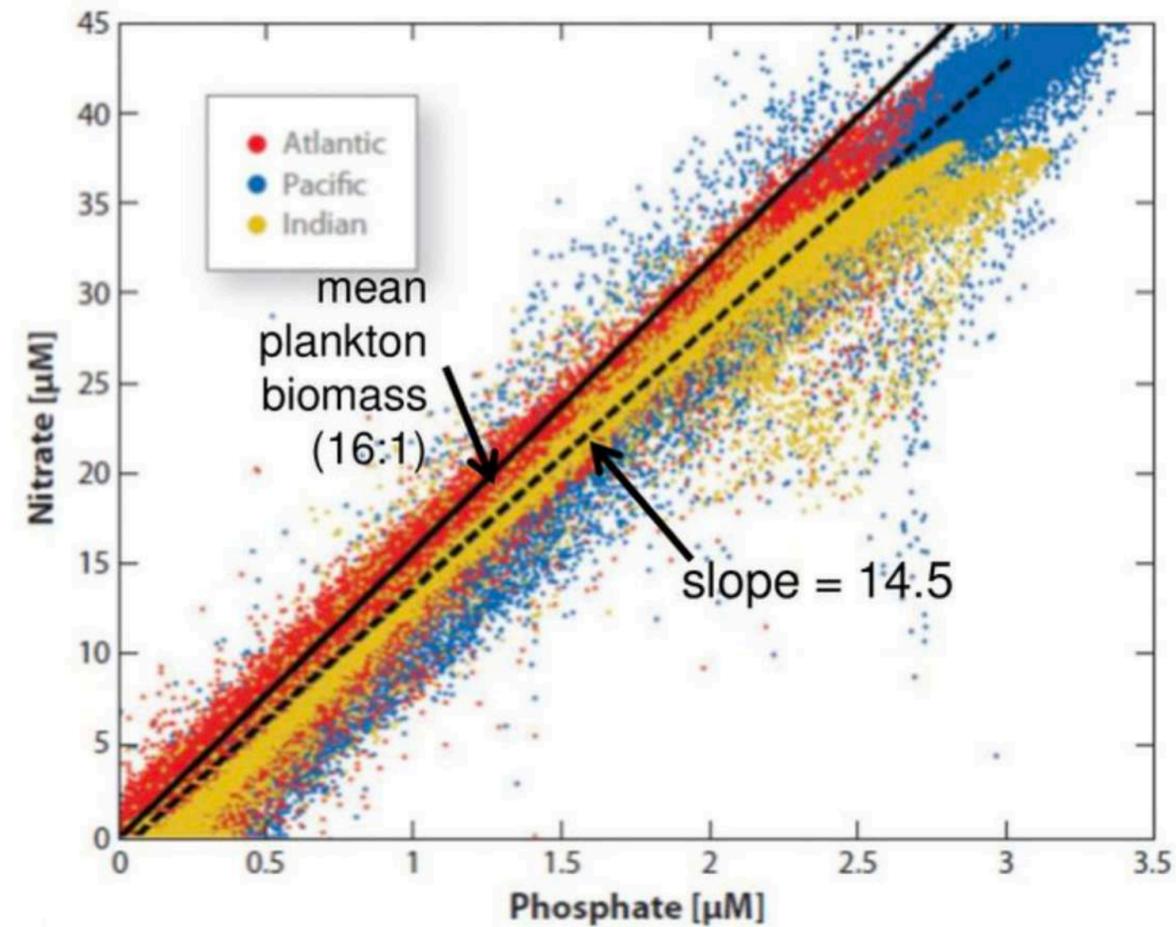
# All is connected

- In 1934, Alfred C. Redfield reported a suite of dissolved nitrate, phosphate and oxygen measurements from various depths in the Atlantic, Pacific and Indian oceans.
- These data showed a remarkable consistency, with **nitrate and phosphate** occurring in a ratio of about 20:1 in most of these samples. Later refined to **16:1**, and expanded to include a ratio of **carbon to phosphate of 106:1**.
- **The Redfield ratio has come to define our understanding of ocean biogeochemical cycling**
- **Biology dictates the availability of nutrients —> carbon to nitrogen to phosphorus is a nearly constant 106:16:1**

# The Redfield ratio



Correlation between concentrations of nitrate and phosphate in the waters of western Atlantic Ocean. Ordinate, concentration of nitrate, units  $10^{-3}$  millimols per liter; abscissa, concentration of phosphate, units  $10^{-4}$  millimols per liter. The line represents a ratio of  $\Delta N : \Delta P = 20 : 1$  milligram atoms.

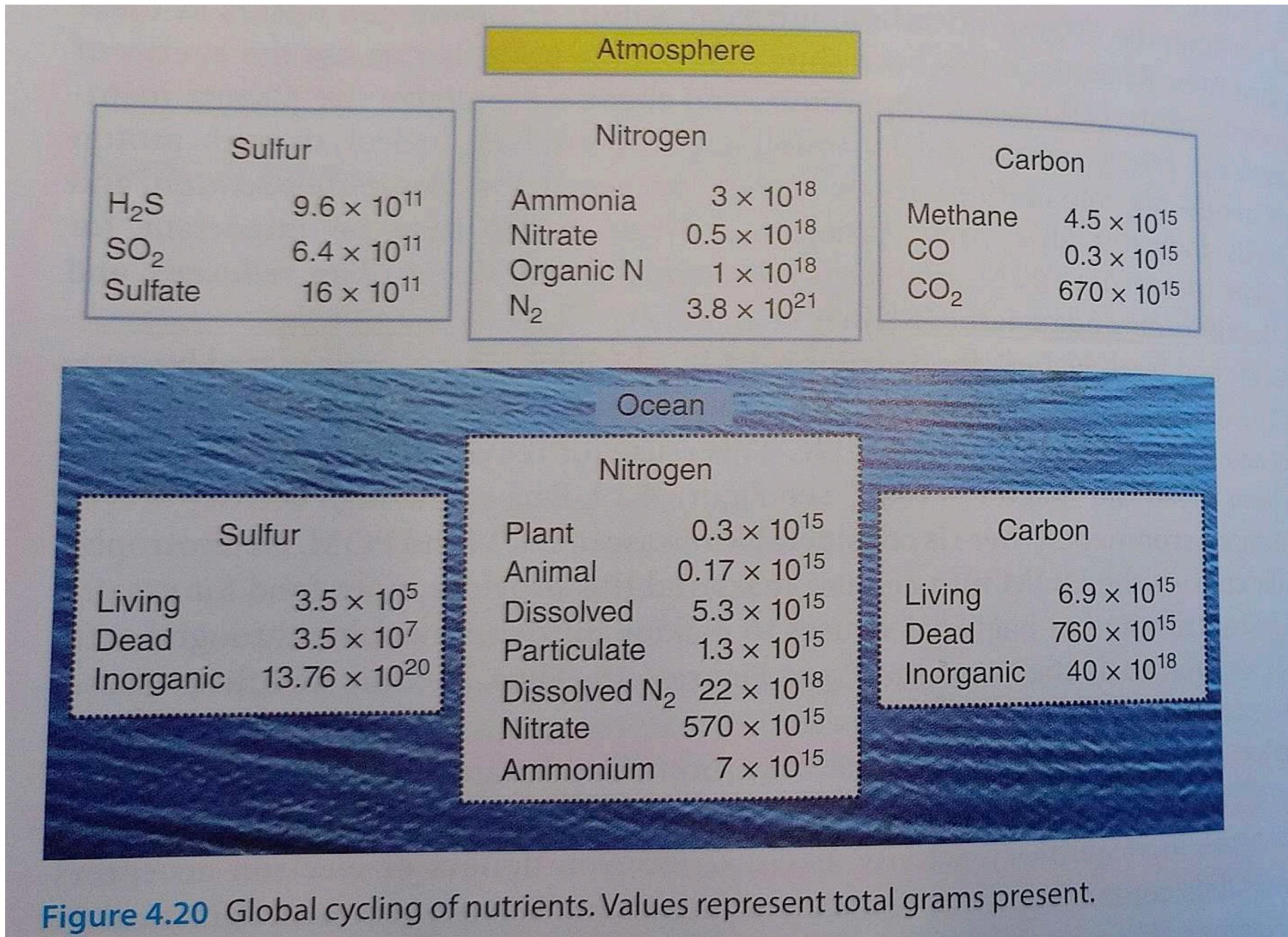


Webber & Dutch; Annu. Rev. Marine. Sci. 2012.4:113-141

# More than the Redfield Ratio

$C_{124,000}N_{16,000}P_{1,000}S_{1,300}K_{1,700}Mg_{560}Ca_{500}Sr_{5.0}Fe_{7.5}Zn_{0.8}Cu_{0.38}Co_{0.19}Cd_{0.21}Mo_{0.03}$ .

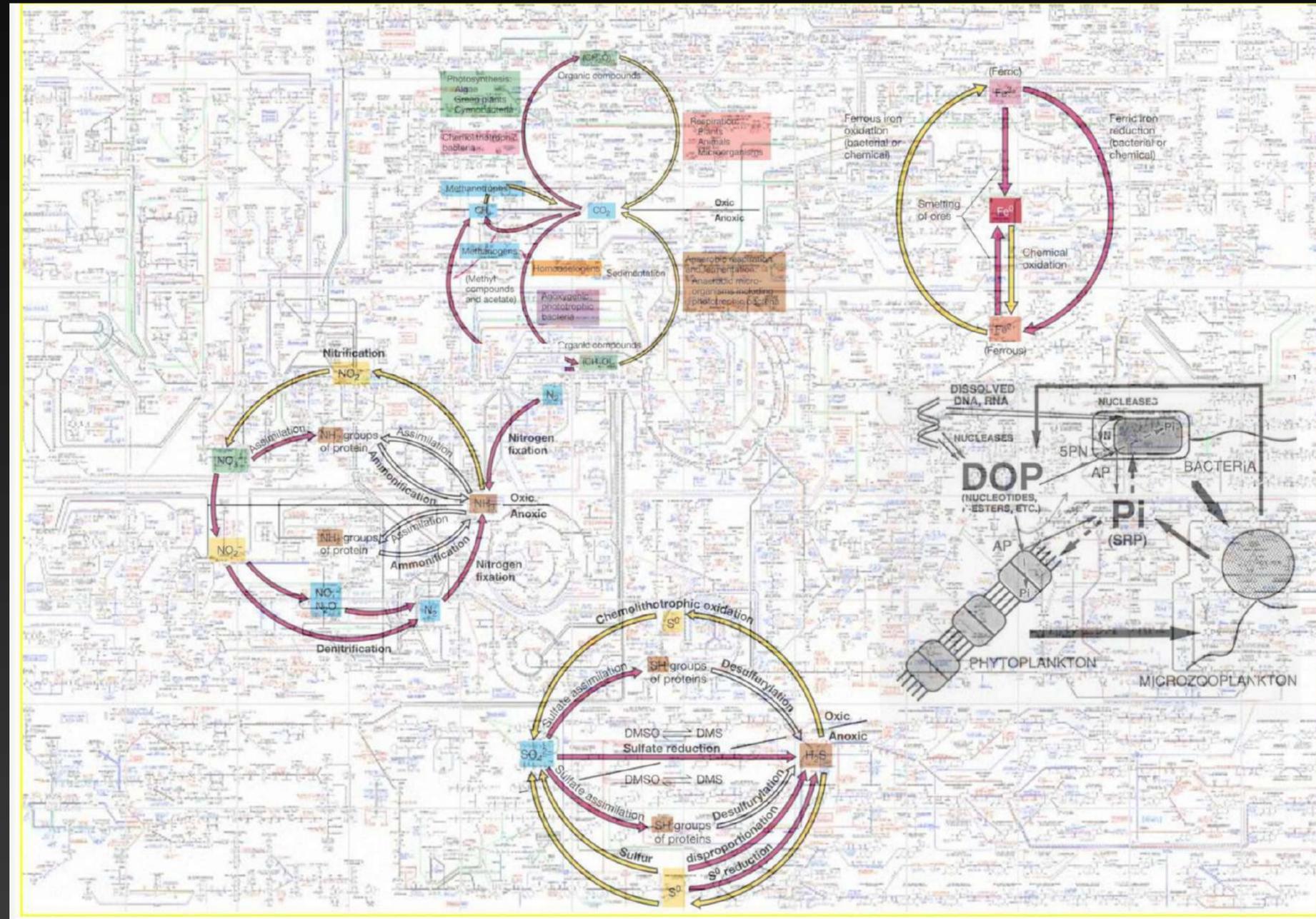
*Ho, T. Y., Quigg, A., Finkel, Z. V., Milligan, A. J., Wyman, K., Falkowski, P. G., & Morel, F. M. (2003). The elemental composition of some marine phytoplankton 1. Journal of Phycology, 39(6), 1145–1159. <https://doi.org/10.1111/j.0022-3646.2003.03-090.x>*



# Unity of biochemistry

Interconnected biogeochemical nutrient cycles

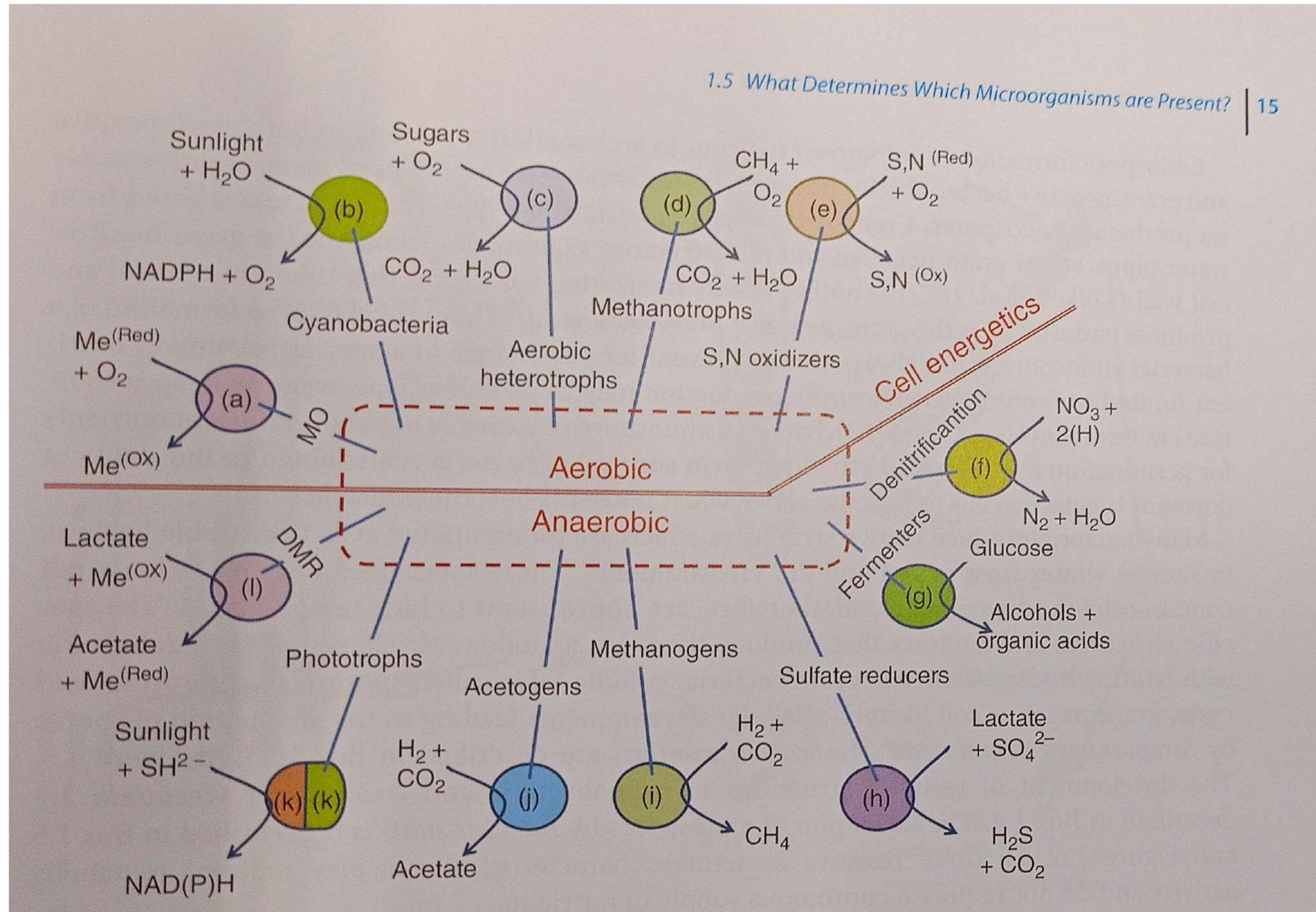
By Farooq Azam



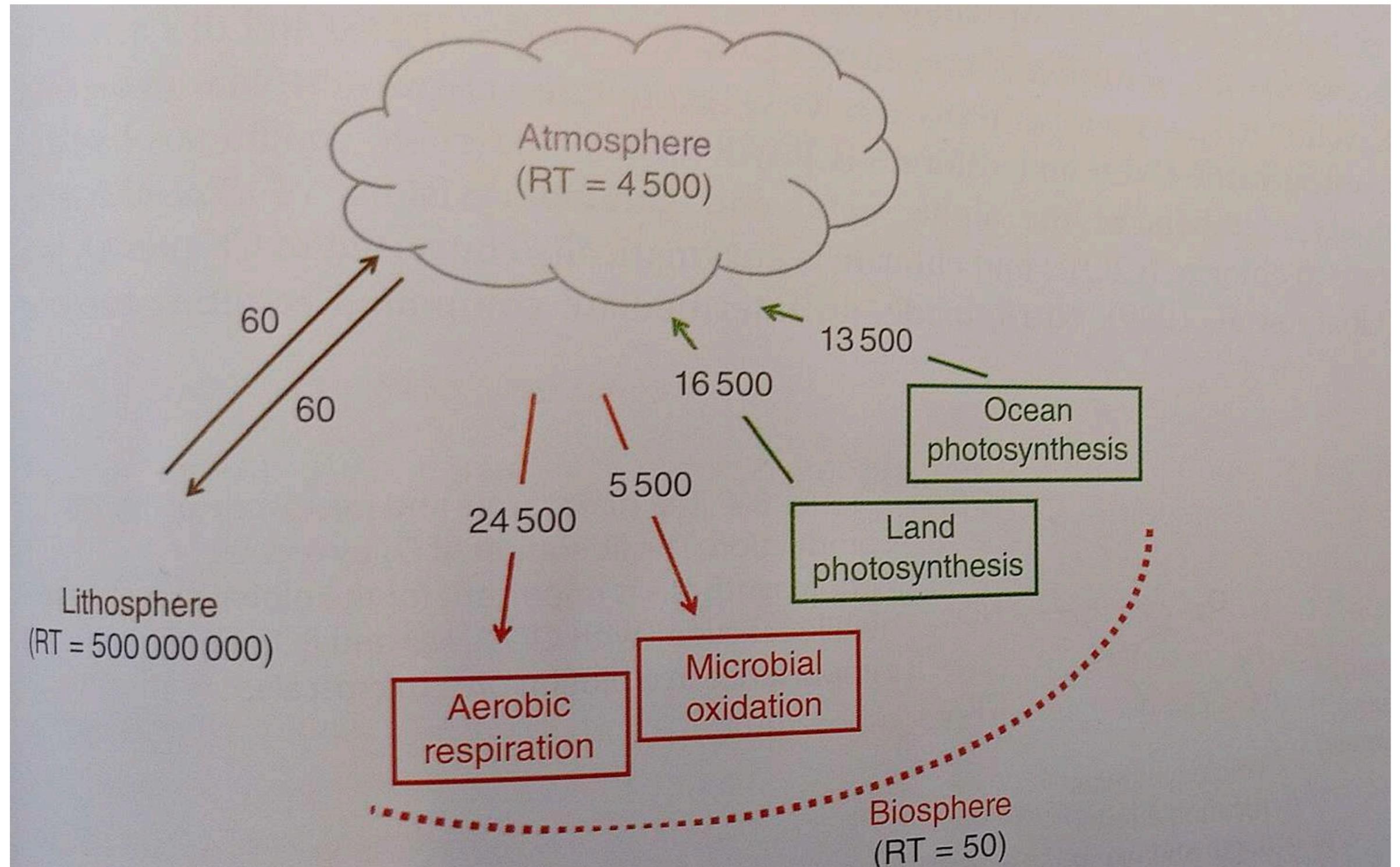
# Phototrophy & Chemotrophy

Aerobic metal oxidizers

Dissimilatory metal reduction



# Oxygen



RT= residence time, yr  
Fluxes:  $10^{10} \text{ O}_2 \text{ kg yr}^{-1}$

# Nitrogen

¥ 12% by dry weight of microbial cell

¥ Proteins & nucleic acid

¥ Diverse redox states:  $\text{NH}_4^+$  (-3),  $\text{N}_2$  (0),  $\text{N}_2\text{O}$  (+1),  $\text{NO}$  (+2),  $\text{NO}_2^-$  (+3),  $\text{NO}_3^-$  (+5)

¥ Nitrogen fixation (*Trichodesmium*, Cyanobacteria symbionts w. Diatoms, tintinnids and radiolarians, primnesiophyte, some Alpha- Gamma -proteobacteria and Planctomycetes, in association w. bivalves in sediment and seeps)

¥ Nitrogen assimilation

¥ Ammonification ( $\text{NO}_2^- \rightarrow \text{NH}_4^+$ )

¥ Nitrification ( $\text{NO}_2^- \rightarrow \text{NO}_3^-$ )

¥ Denitrification ( $\text{NO}_3^- \rightarrow \text{N}_2$ )

¥ Anaerobic ammonia oxidation (annamox)

# Focus on N metabolisms

## \* Nitrification:

### \* Bacteria and Archaea

- ❖ Bacteria: Ammonium oxidation (ammonia monooxygenase, AMO,  $\text{NH}_4^+ \rightarrow \text{NO}_2^-$ ) and then nitrite oxidation (nitrite oxidoreductase, NXR,  $\text{NO}_2^- \rightarrow \text{NO}_3^-$ )
- ❖ Carried by two distinct group of microbes
- ❖ Widely distributed
- ❖ Ammonia oxidizers and nitrite oxidizers
- ❖ Suspended particles, upper oxic sediment layer beneath upwelling areas
- ❖ **VERY IMPORTANT** for organic matter degradation and remineralization
- ❖ *Nitrospira*
- ❖ Bioturbation in sediment for  $\text{O}_2$  availability

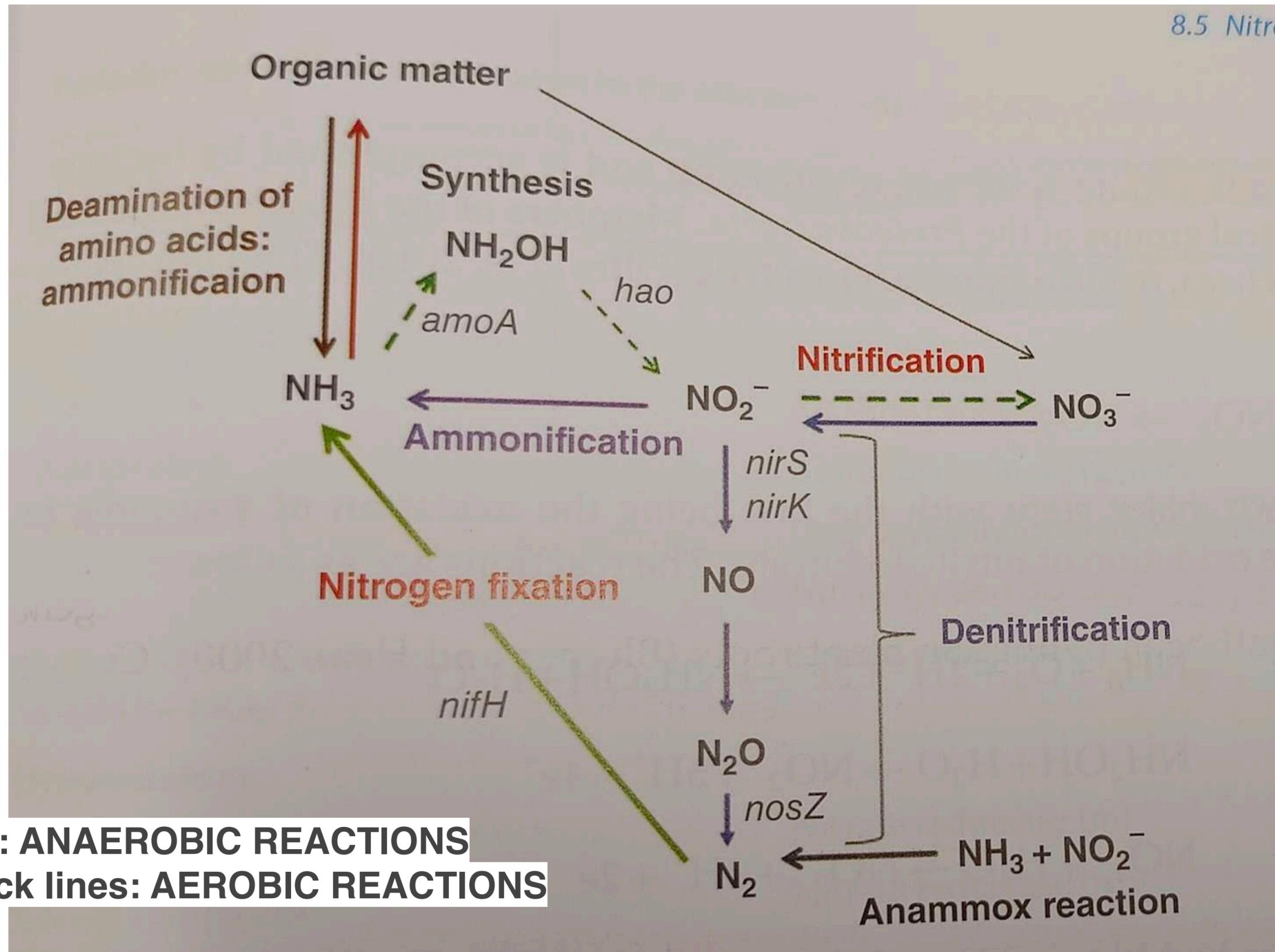
- **Denitrification:** Using  $\text{NO}_3^-$ : dissimulative reduction of nitrate, 4 different enzymes and production of  $\text{N}_2$  —> **loss of N for biology and  $\text{NO}_x$  species (NO and  $\text{N}_2\text{O}$ ) worsening climate warming and acid rain production**

- Denitrification is repressed by  $\text{O}_2$
- Wastewater treatment

## ○ Anaerobic Ammonia oxidation (anammox):

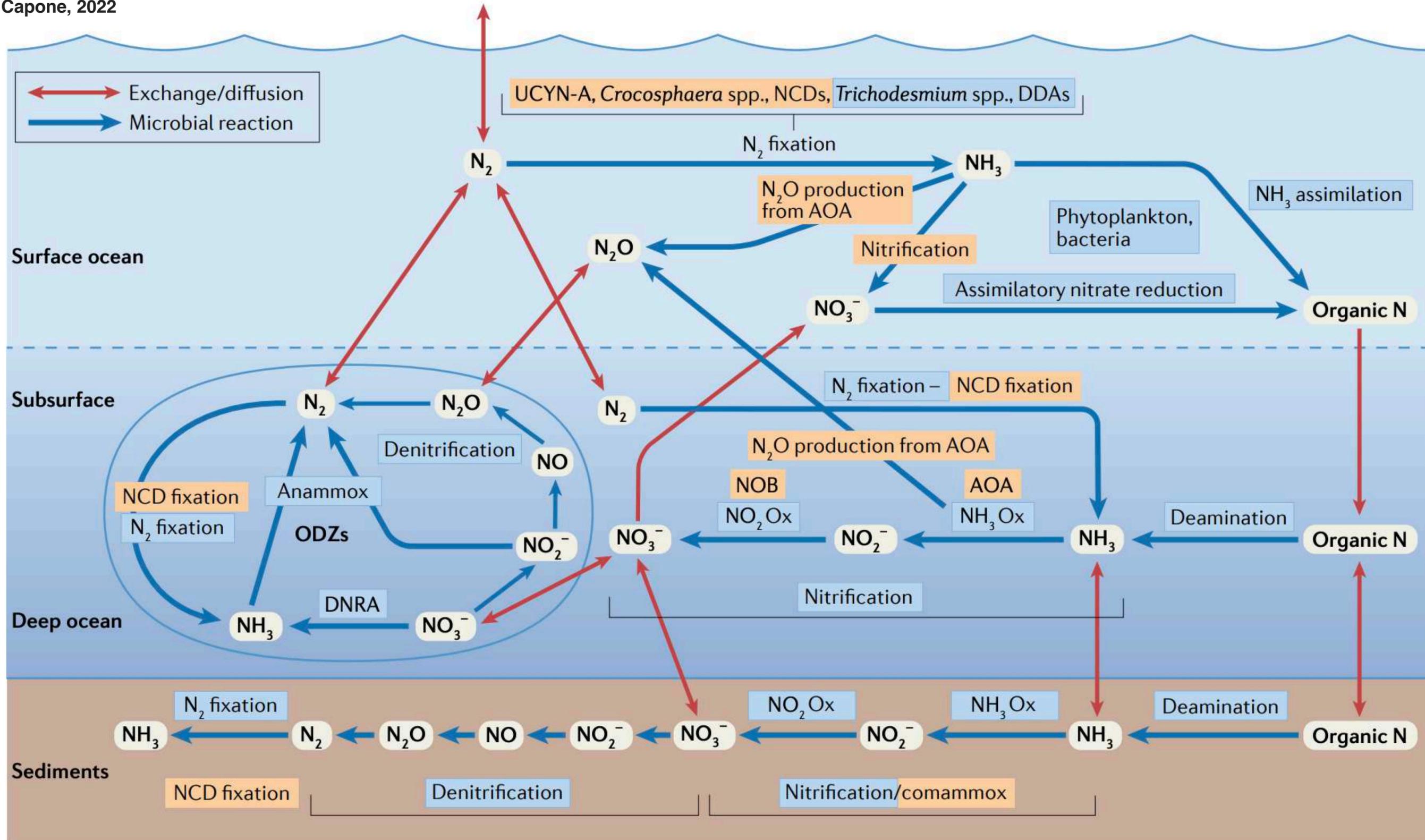
- ❖  $\text{N}_2$  production
- ❖ Planctomycetes
- ❖ Autotrophic,  $\text{CO}_2$

# Nitrogen



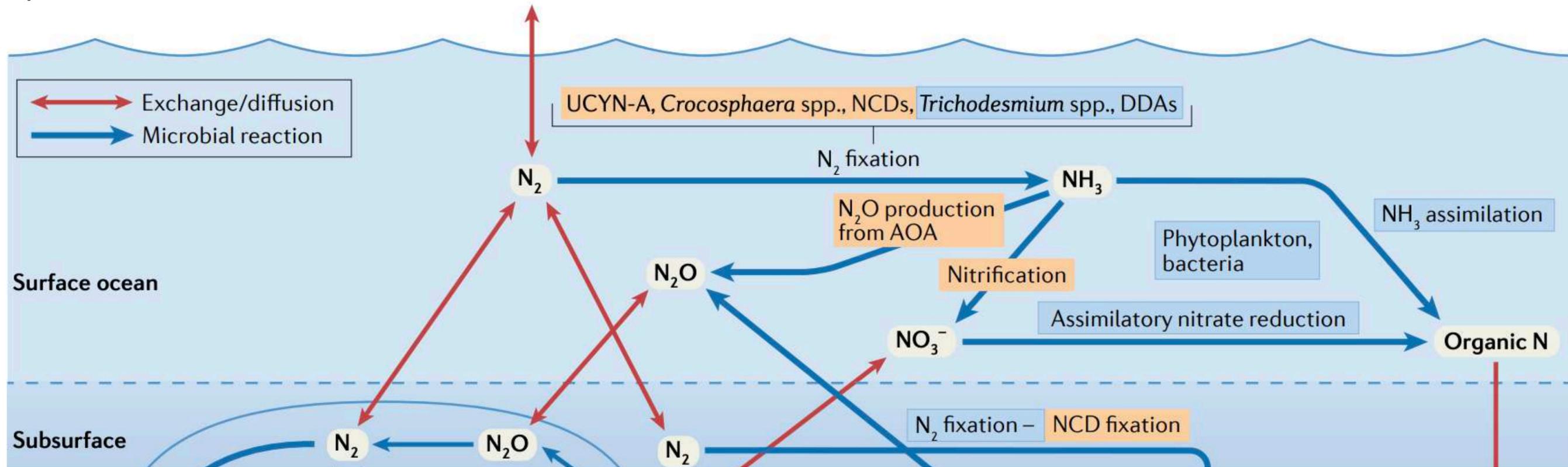
- Solid lines: ANAEROBIC REACTIONS
- Broken stick lines: AEROBIC REACTIONS

# Nitrogen



ODZs, O<sub>2</sub> depleted zones, AOA, ammonia-oxidizing archaea; DDA, diatom–diazotroph association; DNRA, dissimilatory nitrate reduction to ammonia; NCD, non-cyanobacterial diazotroph; NOB, nitrite-oxidizing bacteria; Ox, oxidation; UCYN-A, unicellular cyanobacteria group A

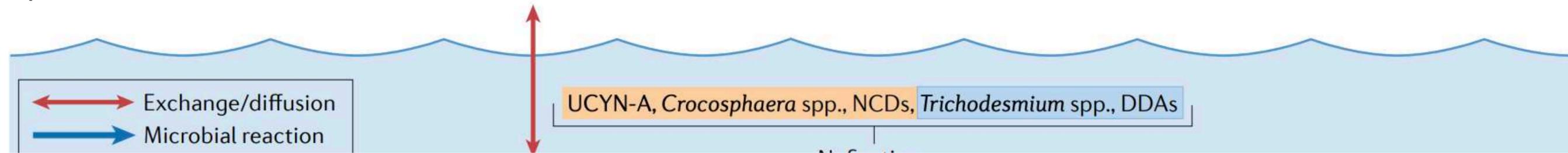
# Nitrogen



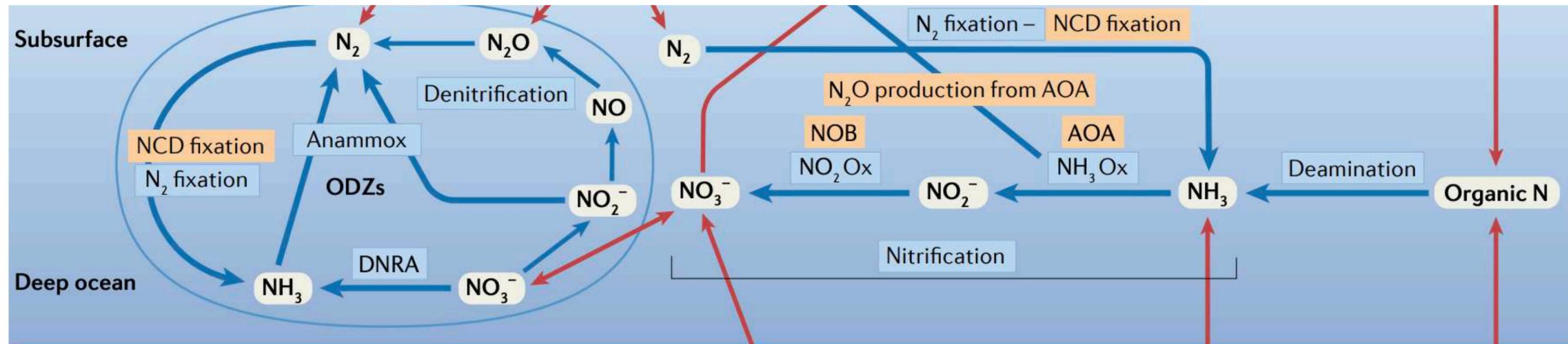
The upper sunlit (photic) ocean, typically the upper 100 m or less, where photosynthesis occurs along with **assimilatory processes such as nitrogen fixation, nitrate reduction and ammonia uptake**

ODZs, O<sub>2</sub> depleted zones, **AOA, ammonia-oxidizing archaea; DDA, diatom–diazotroph association**; DNRA, dissimilatory nitrate reduction to ammonia; NCD, non-cyanobacterial diazotroph; NOB, nitrite-oxidizing bacteria; Ox, oxidation; **UCYN-A, unicellular cyanobacteria group A**

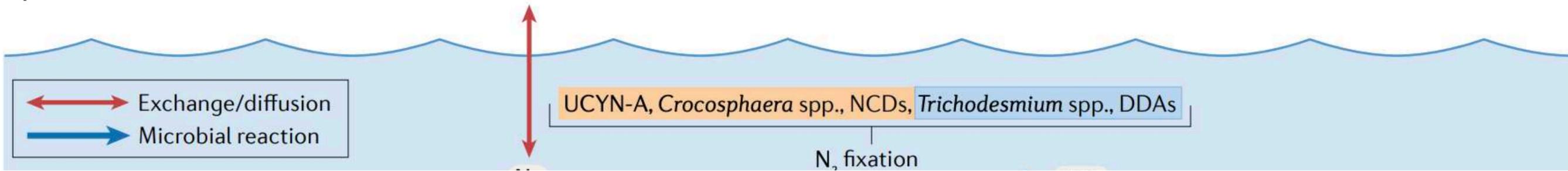
# Nitrogen



The subsurface aphotic and largely **oxic water** column down to the deep sea, where **heterotrophic nitrogen-regenerative (i. e., deamination) and chemoautotrophic pathways, such as nitrification, predominate**; the **anoxic water** column pockets or O<sub>2</sub>-depleted zones (ODZs), where **anaerobic metabolic pathways, such as dissimilatory nitrate reduction, denitrification and anammox**, predominate



ODZs, O<sub>2</sub> depleted zones, AOA, ammonia-oxidizing archaea; DDA, diatom–diazotroph association; DNRA, dissimilatory nitrate reduction to ammonia; NCD, non-cyanobacterial diazotroph; NOB, nitrite-oxidizing bacteria; Ox, oxidation; UCYN-A, unicellular cyanobacteria group A



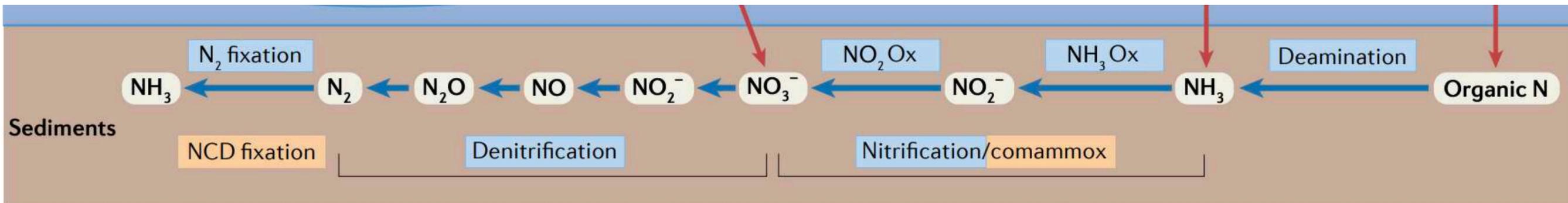
The benthic or seafloor environment: in shallow coastal areas, the benthic environment intersects the photic zone with a similar array of processes to the photic water column.

**Deep ocean's benthic environments are aphotic and dominated by heterotrophic and chemoautotrophic processes.**

Where the organic flux to the sediments is high (for example, on continental shelf sediments), **O<sub>2</sub> diffusing into the sediments is rapidly consumed and depleted, and anaerobic processes predominate**

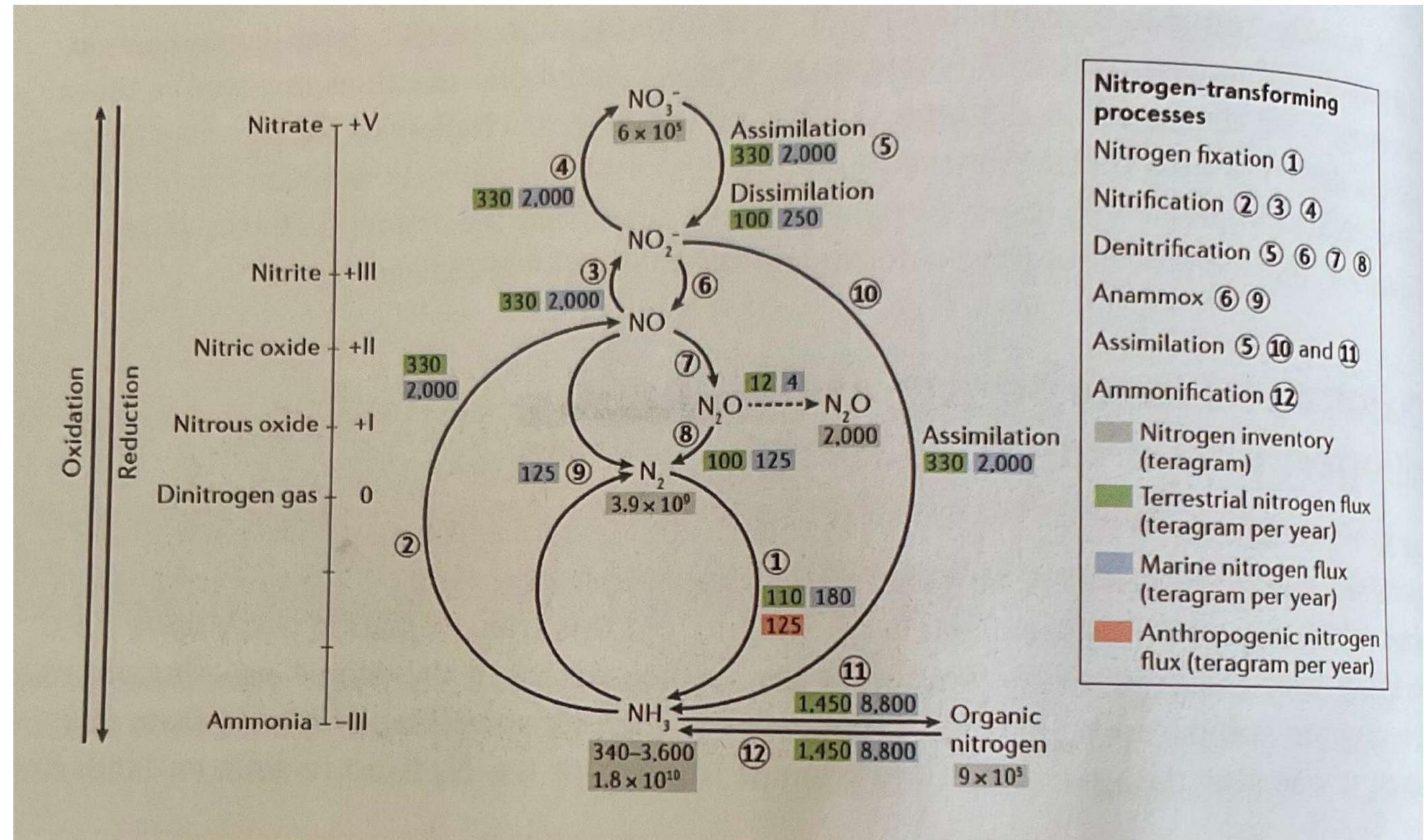
ODZs, O<sub>2</sub> depleted zones, AOA, ammonia-oxidizing archaea; DDA, diatom–diazotroph association; DNRA, dissimilatory nitrate reduction to ammonia; **NCD, non-cyanobacterial diazotroph**; NOB, nitrite-oxidizing bacteria; Ox, oxidation; UCYN-A, unicellular cyanobacteria group A

# Nitrogen



# Nitrogen cycle

- $N_2$  is 78% of atmosphere
- $N_2$  must be fixed in a reduce status for life
- Diazotrophy  $\sim 180\text{-}200 \text{ M y}^{-1}$
- Diazotrophy in tropical & subtropical ocean
- Diazotrophy  $\gg$  on land and  $\gg$  industrial production of  $NH_3$
- Denitrification at 100-1000 m in Indian Ocean and eastern tropical Pacific Ocean



Munn, 2011

# Nitrogen cycle

- ¥ N remineralization= ammonification & nitrification
- ¥ Ammonification:  $N_2 \rightarrow NH_3$ , highly reduced form, less energy for uptake for making aa, by many microbes, including fungi
- ¥  $NH_3$  used immediately
- ¥ Nitrification: oxidation of ammonia to nitrite (by AOA, AOB) and then oxidation of nitrite to nitrate for making biomass (microbes and phytoplankton)
- ¥  $N_2$  Loss: half of global loss  $N_2$  in OMZ
- ¥ Denitrification at 100-1000m in Indian Ocean and eastern tropical Pacific Ocean, anaerobic respiratory pathway
- ¥ Anammox in anoxic sediment

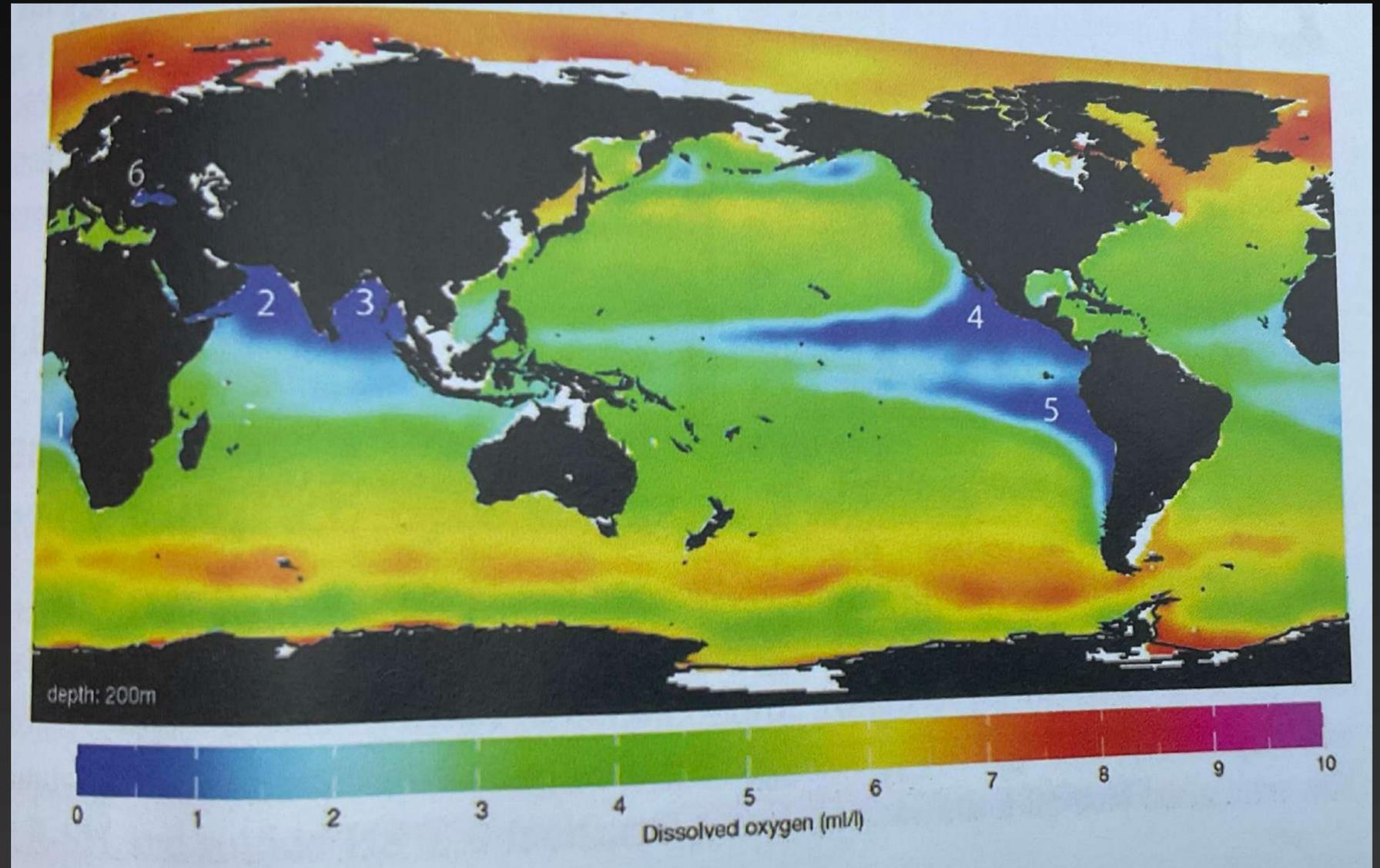
# Oxygen Minimum Zones

OMZ 200 m

- 1 SW African continental margin
- 2 Arabian Sea
- 3 Bay of Bengal
- 4 E tropical N Pacific
- 5 E tropical S Pacific
- 6 Black Sea

1000-1500 m

Heterogenous water mass

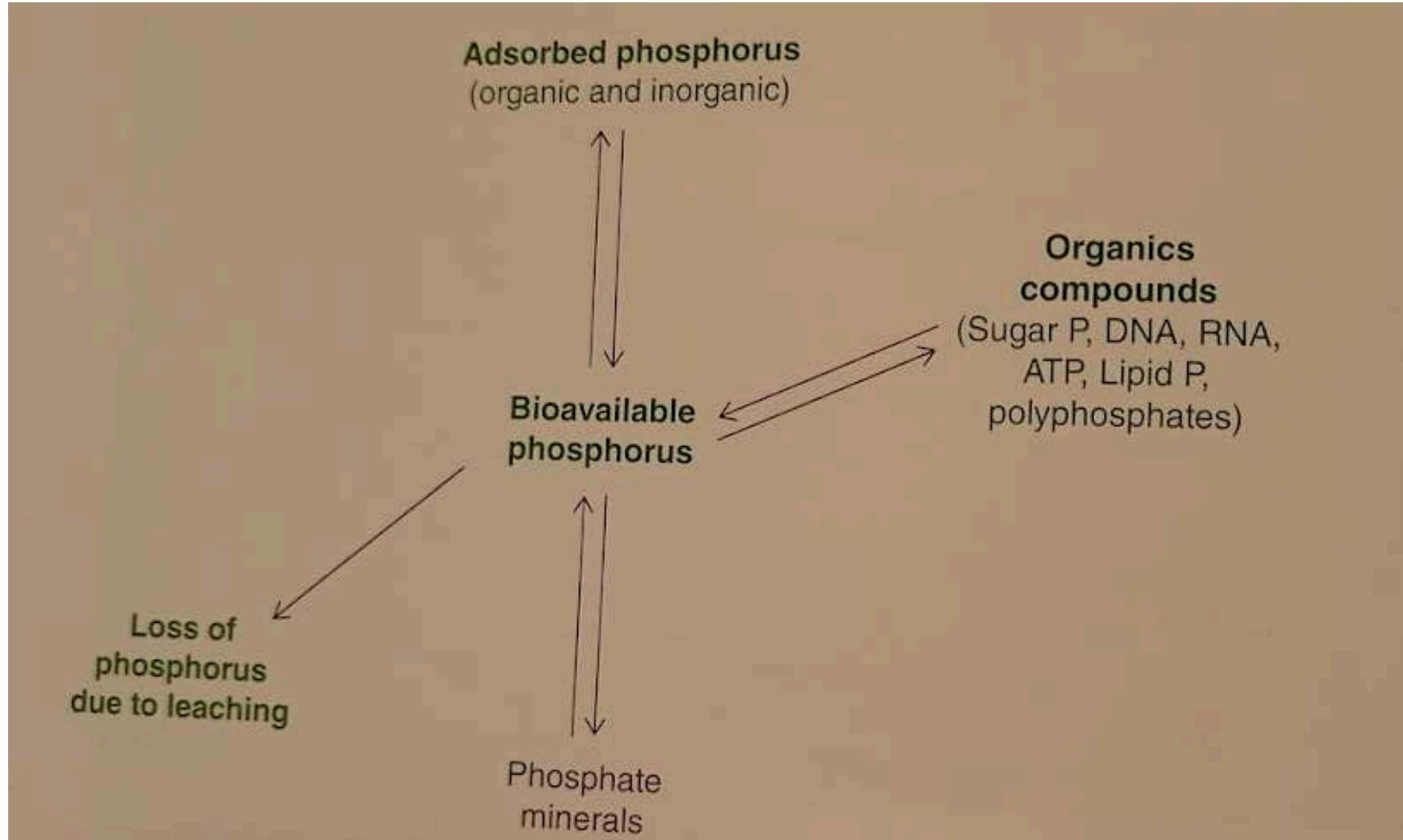


Munn, 2011

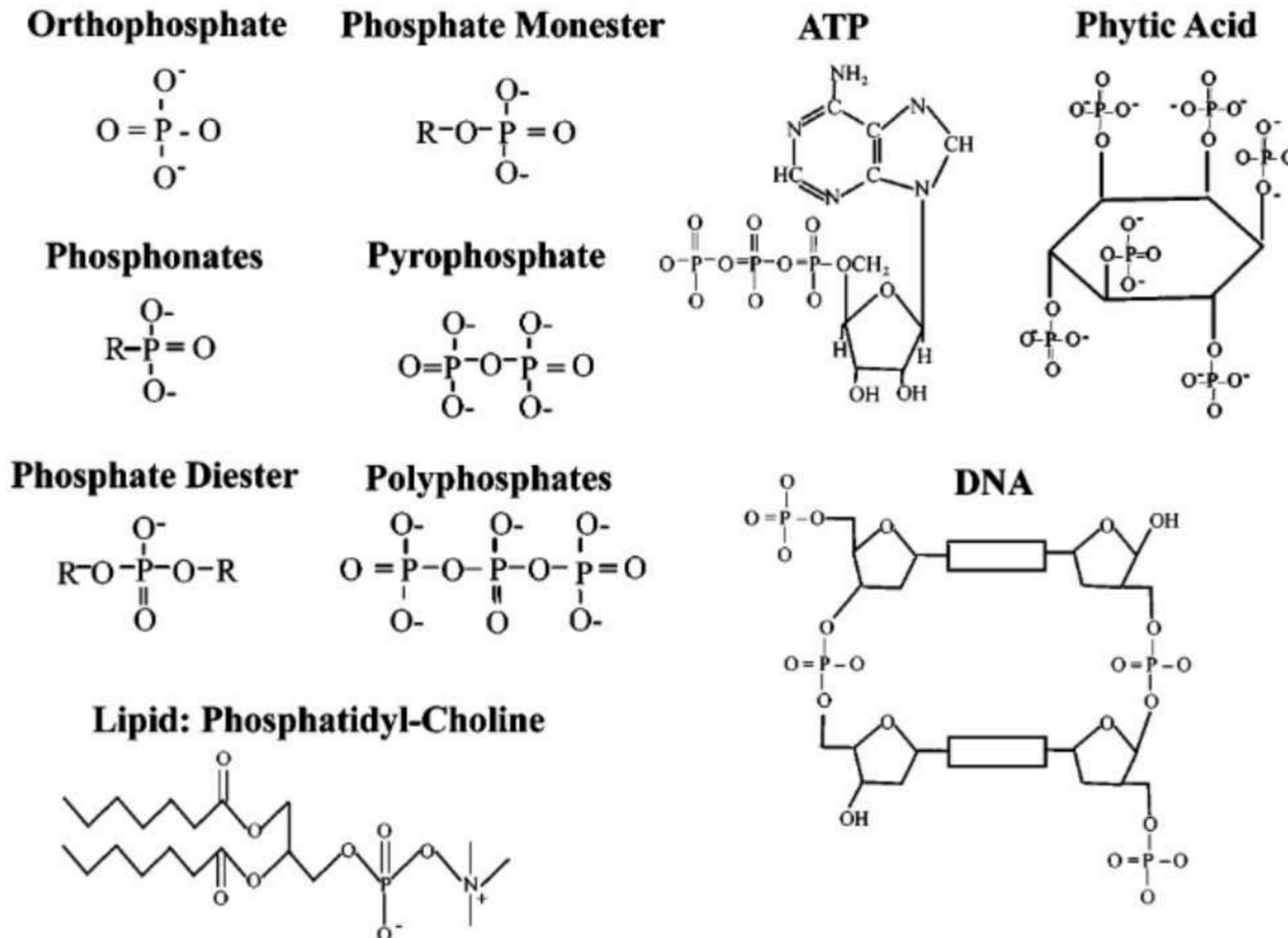
# Phosphorus

- Nucleic acid, ATP and phospholipids
- P cycle on land influence P cycle in ocean
- Limiting or co-limiting element
- Sole input is terrestrial runoff
- P sink is burial in sediment
- No gas beside phosphine ( $\text{PH}_3$ )
- Dissolved organic (DOP) and inorganic (DIP) pools in ocean

# Phosphorus fate in the ocean

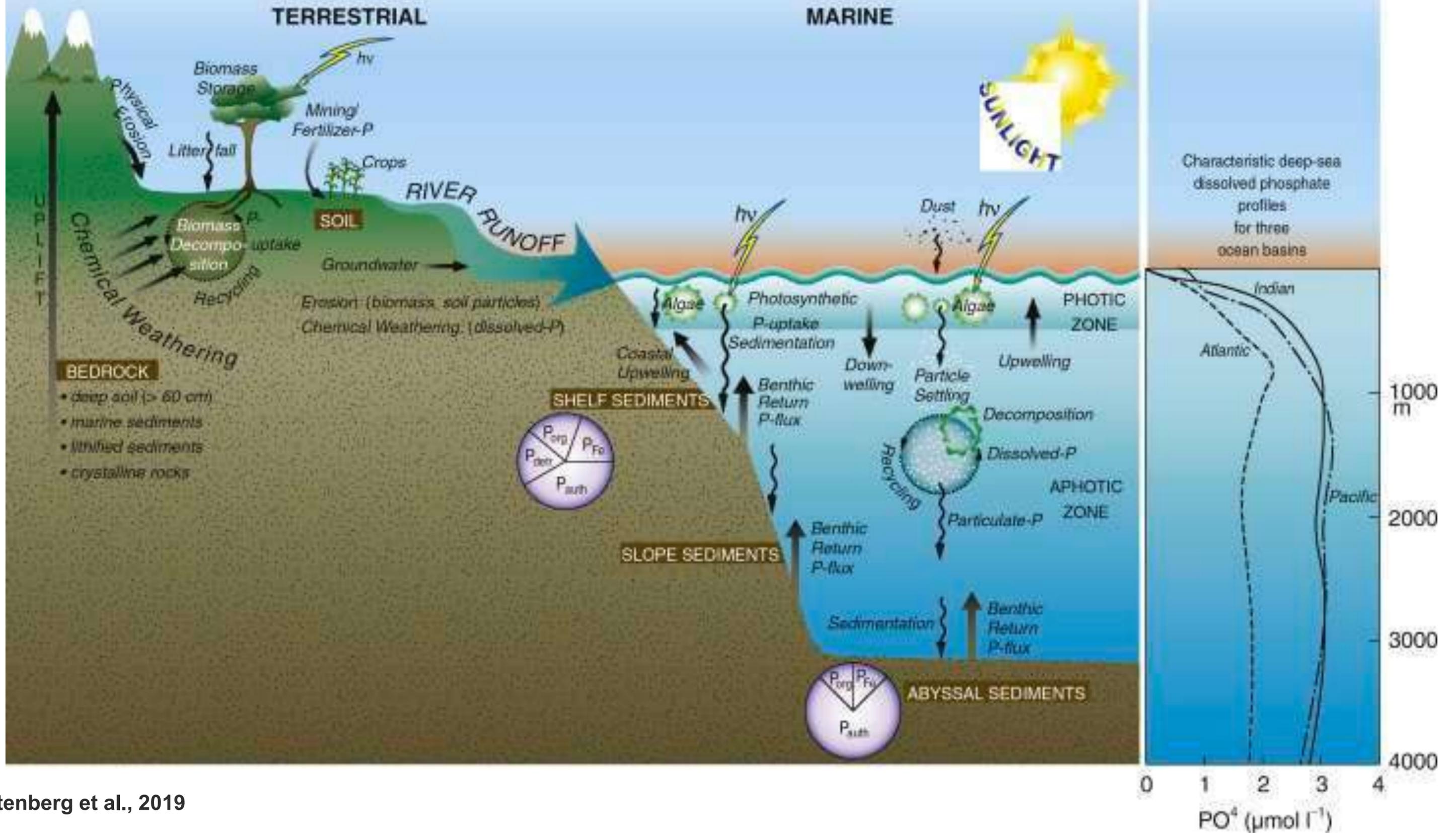


# Phosphorus rich molecules



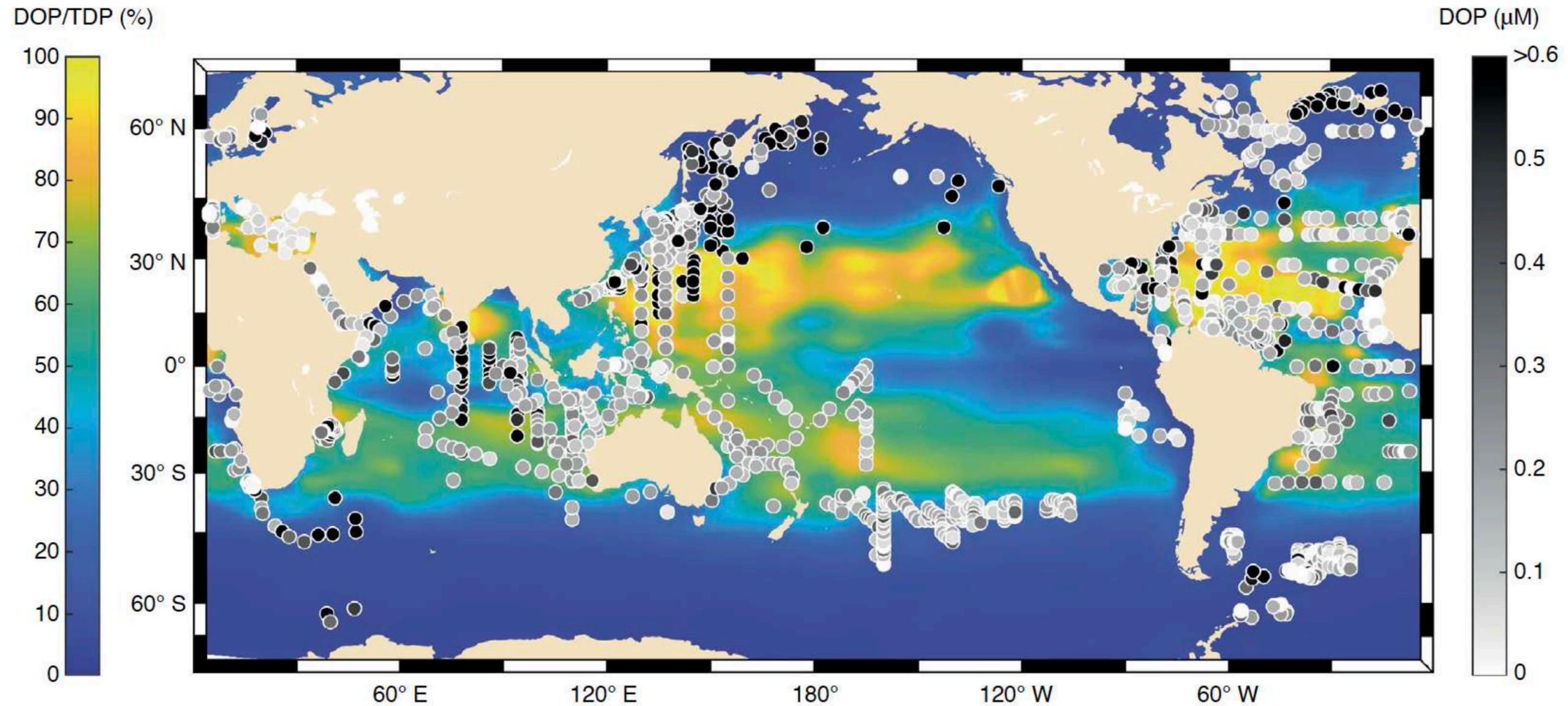
**Figure 1.** Biologically important compounds.

# THE GLOBAL PHOSPHORUS CYCLE



# Distribution of Dissolved Organic Phosphorus and Total Dissolved Phosphorus

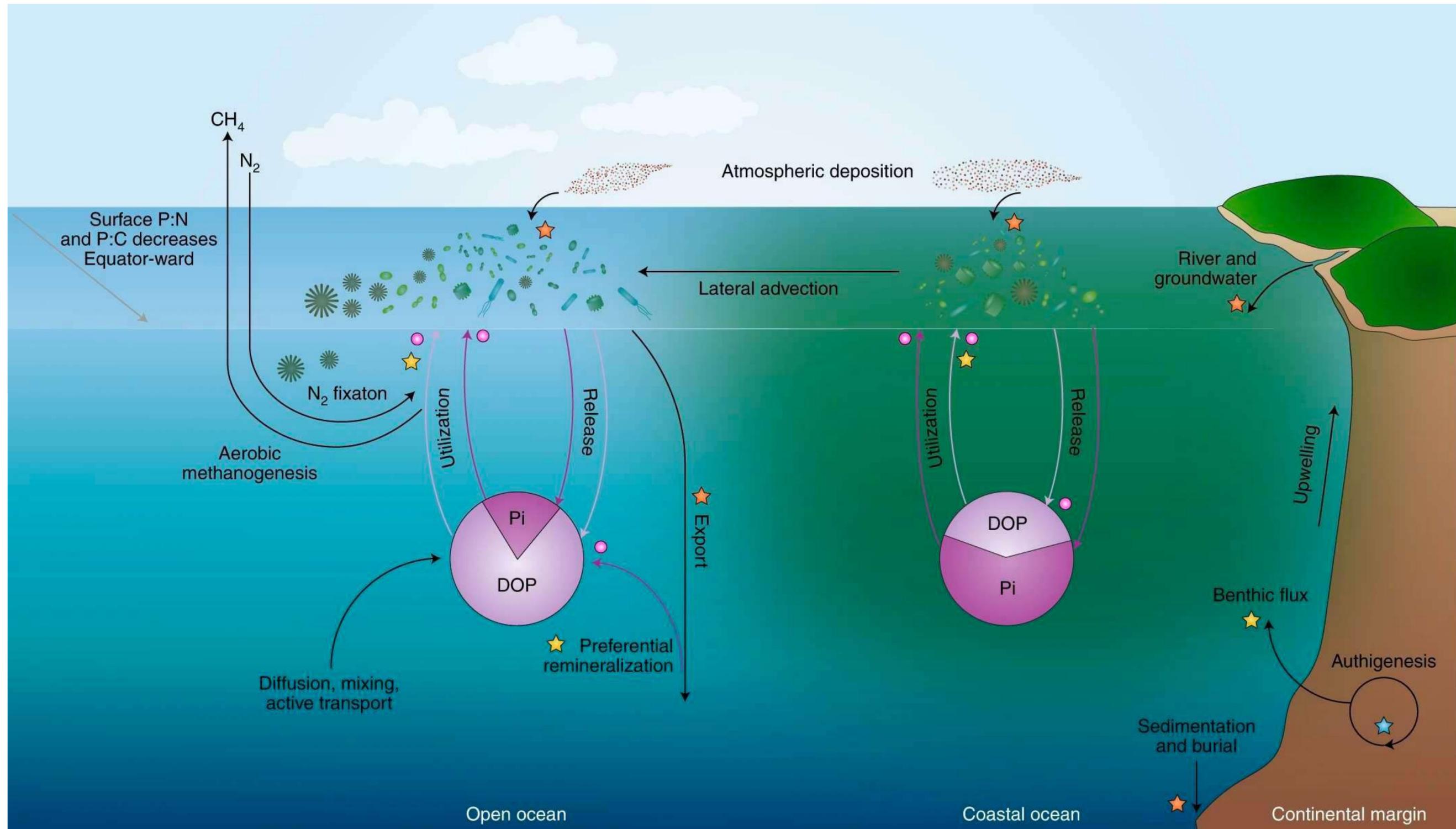
Dunhamel et al., 2021



**Fig. 2 | Distribution of DOP concentrations and contribution to TDP over the global ocean.** Percentage contribution (colour bar) of DOP to TDP and observed DOP concentrations (greyscale circles) at 50 m depth. DOP contributions to TDP were mapped using both modelled DOP data from ref. <sup>28</sup> and soluble reactive P (SRP) from the GLODAPv2\_2016 climatology<sup>99</sup>. Note the sparse DOP measurements.

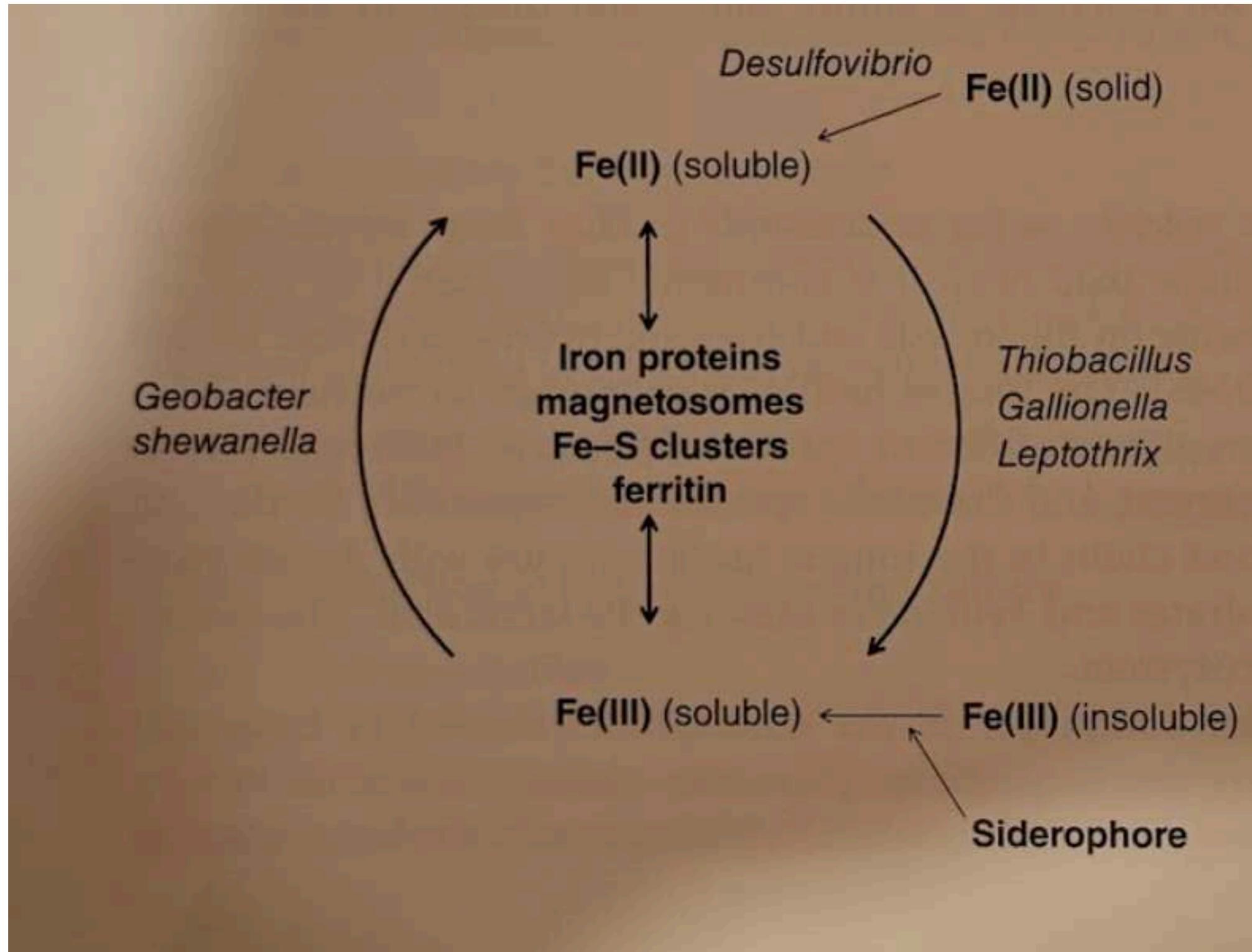
# Phosphorus

- Microbes can use DOP and DIP
- DOP more labile than DOC and DOC
- DOP can be described as a continuum of labile, semi-labile and refractory forms
- DOP is poorly characterized at the molecular level, yet operationally includes organic and inorganic polymeric forms of P within three main bond classes: P-esters (including mono (P–O–C) and diesters (C–O–P–O–C)), P-anhydrides or polyphosphates (P–O–P) and phosphonates (P–C)
- DOP >> Pi in oligotrophic gyres
- DOP as phosphonate, stable C-P bonds
- Synthetic phosphonates such as herbicides, insecticides and detergent additives



**Interactions with metals** are indicated by stars, including mineral-adsorbed P (orange star), metal-associated P precipitation (blue star) and metal-associated P hydrolysis (yellow star). **Processes involving reduced-P compounds** are shown as pink circles. In the surface ocean, **particulate P:N and P:C ratios decrease with latitude** (grey arrow)

# Iron



Coordination chemistry that makes siderophores so effective at iron scavenging

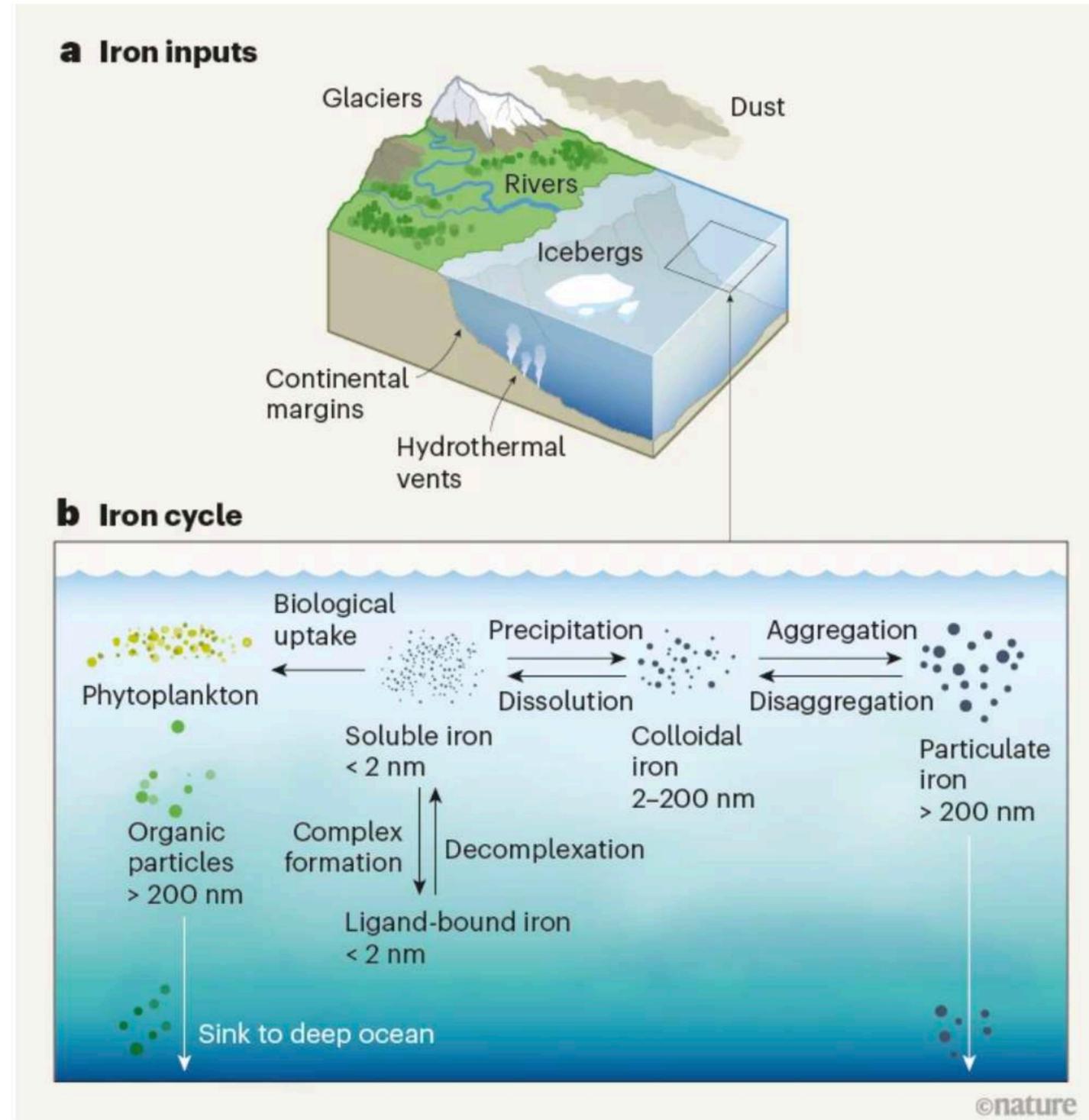
Siderophores **bind Fe<sup>3+</sup> (ferric iron) – not Fe<sup>2+</sup> (ferrous iron)**.

The ligand atoms in the siderophore (like hydroxamates, catecholates, or carboxylates) strongly stabilize Fe<sup>3+</sup> through coordinate covalent bonds

This binding actually *helps keep iron in the ferric state* because the Fe<sup>3+</sup>–ligand complex is thermodynamically very stable

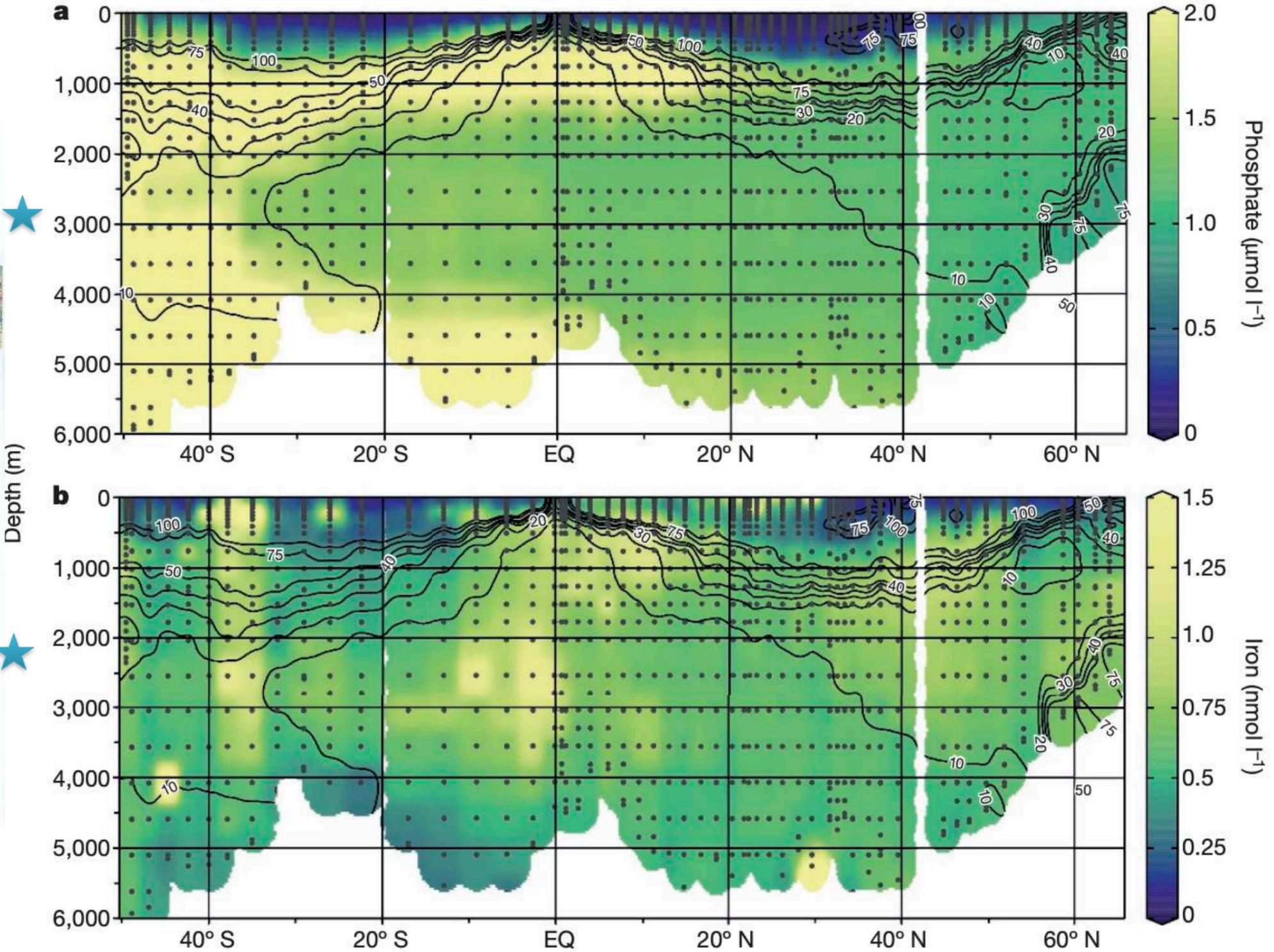
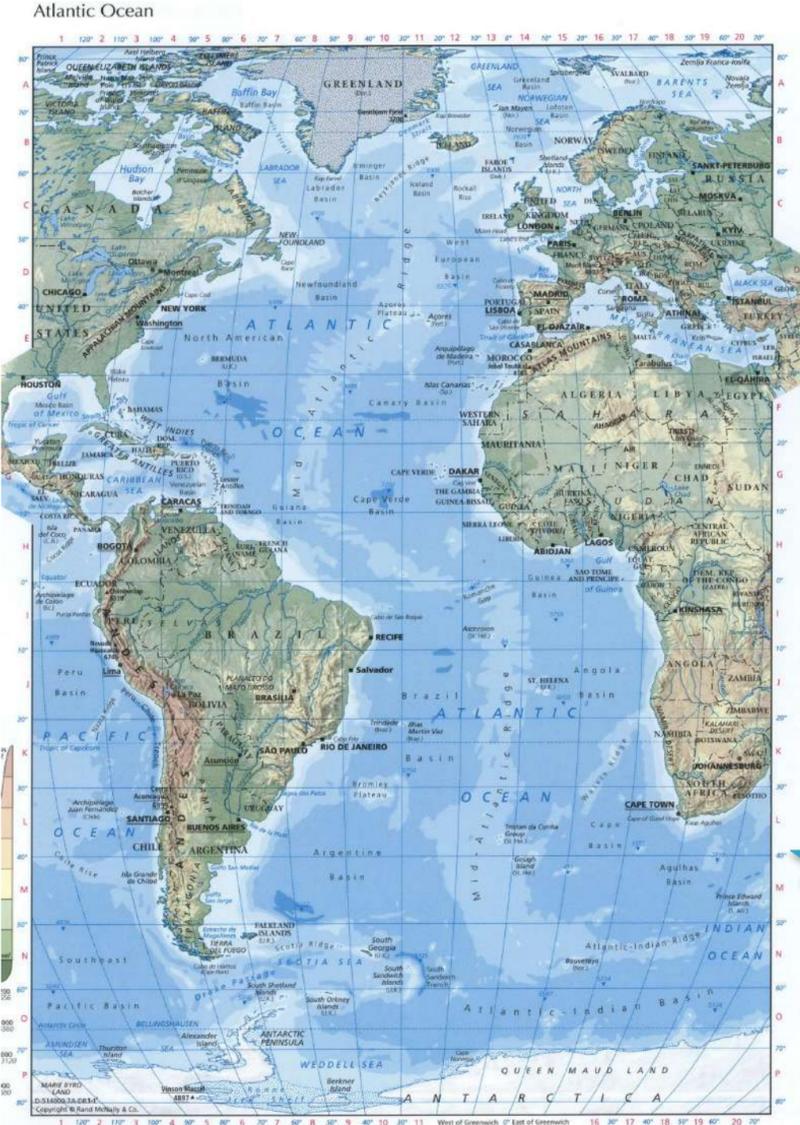
# Iron

- Essential element
- $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  redox state
- Terrestrial run off
- Dust
- Volcanic ash
- Hydrothermal vents
- Melting glacier ice
- Bioavailable Fe is  $\ll$  in SW due to low solubility caused by pH  $\sim$ 8 Majority of Fe is bound to organic matter
- Siderophores to acquire Fe
- HNLC zone



Toner, 2023  
Tagliabue, A. et al. Nature 620, 104–109 (2023)

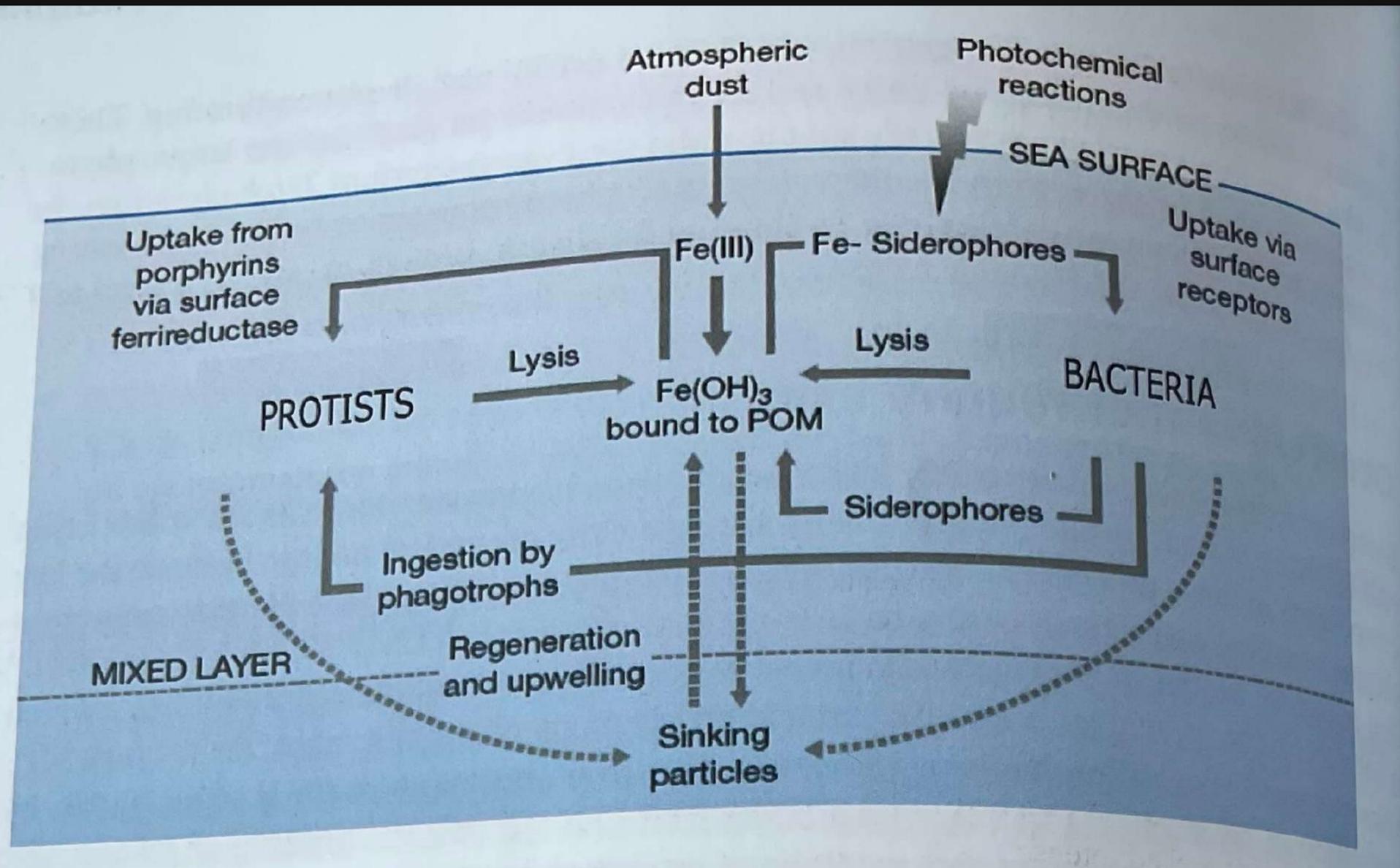
# Observations from a meridional section in the west Atlantic Ocean as a function of latitude and depth



Tagliabue et al., 2017

# Fe

Grazing → low pH vacuole redox of Fe → bioavailable



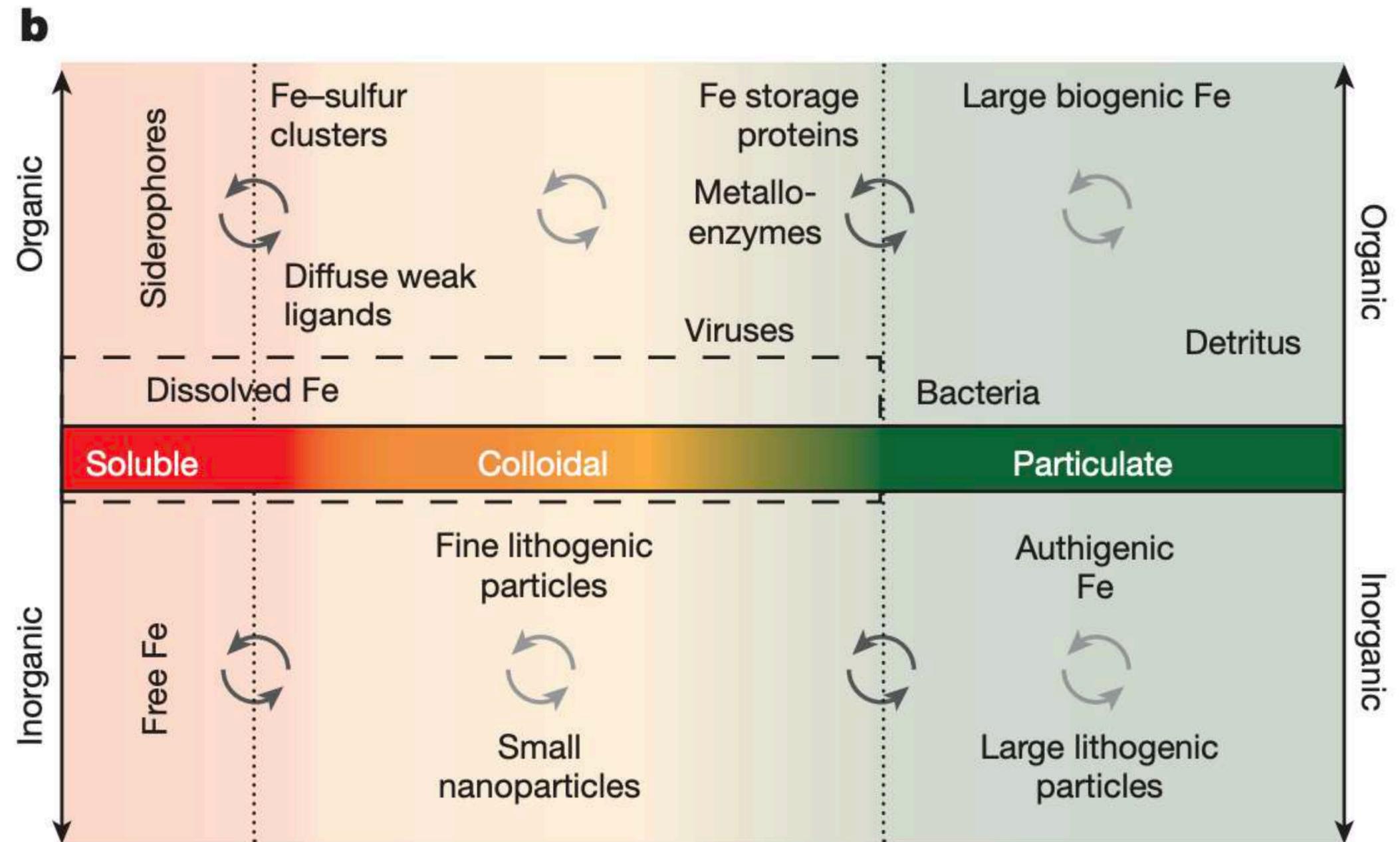
- Feces of whale and birds are point source of Fe
- HNLC and J. Martin
- Bioengineering
- Ferrous wheel

Munn, 2011

# The iron pool continuum

A fluid continuum of soluble, colloidal and particulate iron, as well as the role of inorganic (nanoparticles, authigenic iron and lithogenic species) and organic components: biogenic pools and biomolecules that **bind iron strongly**, as well as **weaker diffuse iron-binding ligands** such as hemes, saccharides or fulvic acids

Authigenic mineral assemblages are a result of a series of dehydration and desilicification reactions during progressive burial, in the present place



Tagliabue et al., 2017

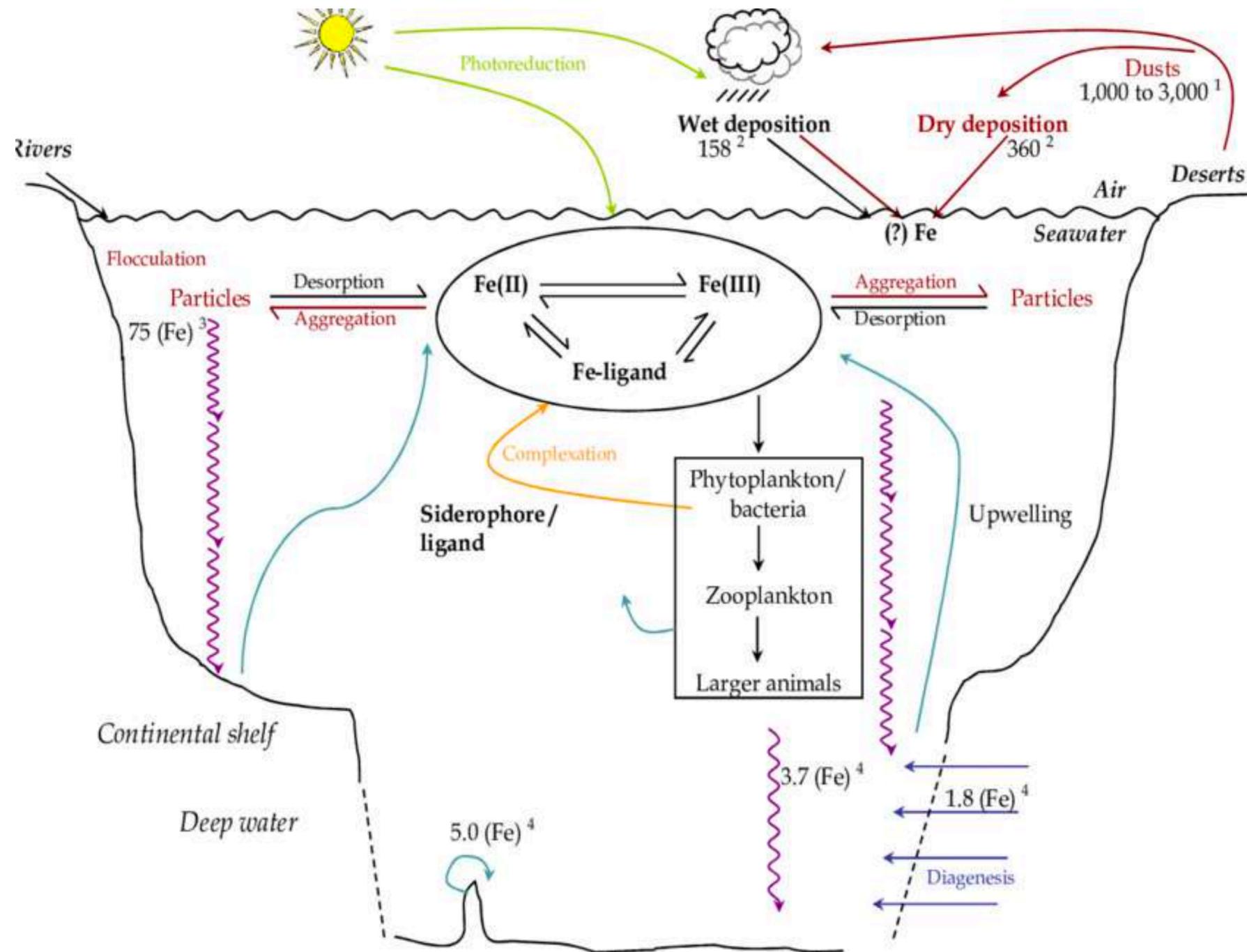
# The marine biogeochemical cycle of iron

Blue arrows:  
resuspension

Purple arrows:  
sedimentation

Black  
compartment:  
dissolved iron

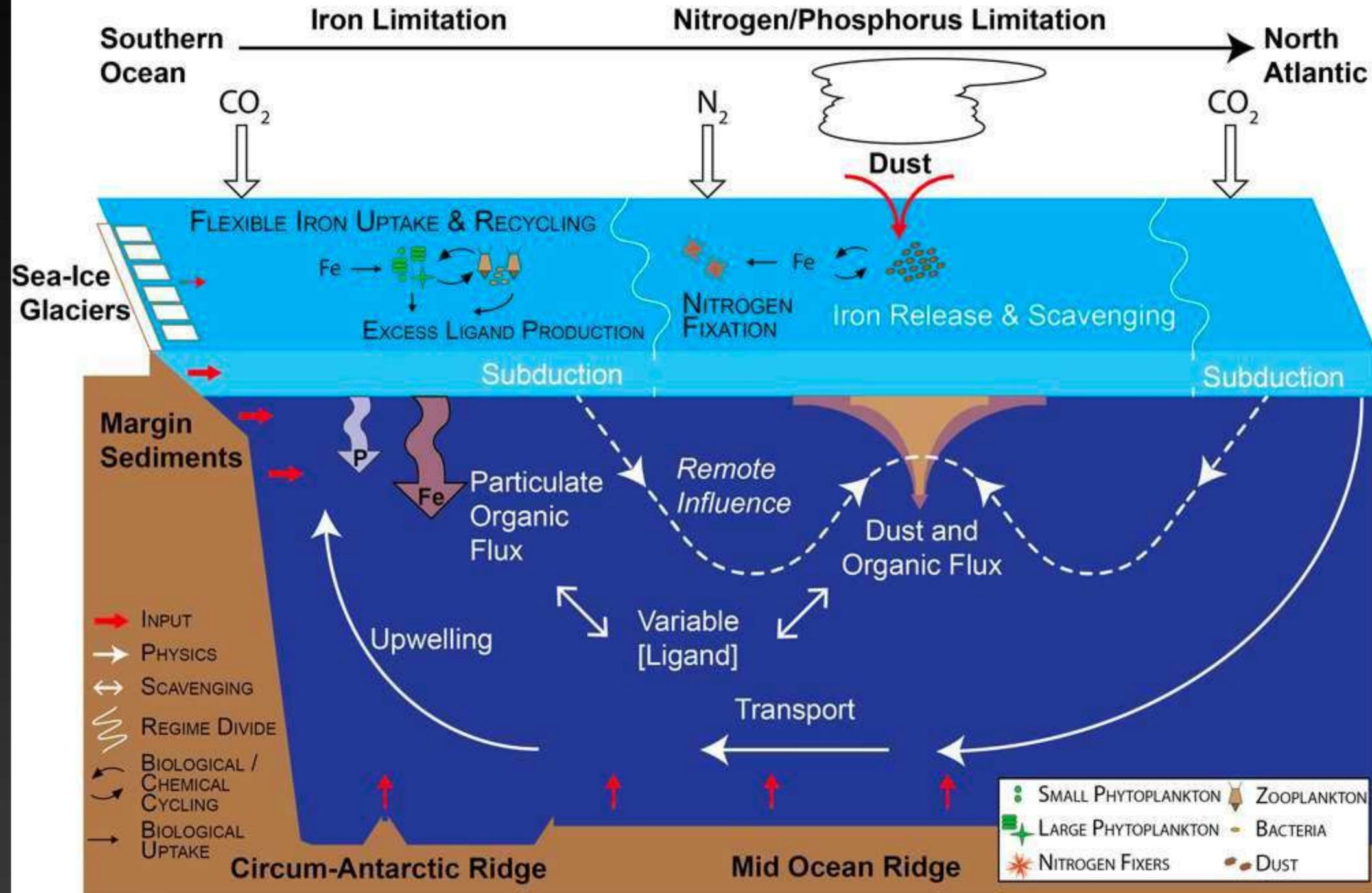
Brown  
compartment:  
particulate iron



Units:  $10^{12} \text{ g yr}^{-1}$

From: Goudie (2008), Jickells and Spokes (2001), Chester (2000), de Baar and de Jong (2001) (Seguret, 2009)

# Fe cycle



## Global scale Fe cycle

Broad meridional contrast between the iron-limited Southern Ocean and the major nutrient-limited low-latitude regimes

Dust remains a dominant source in the low latitudes, but continental margin and upwelled hydrothermal sources are more important in the Southern Ocean

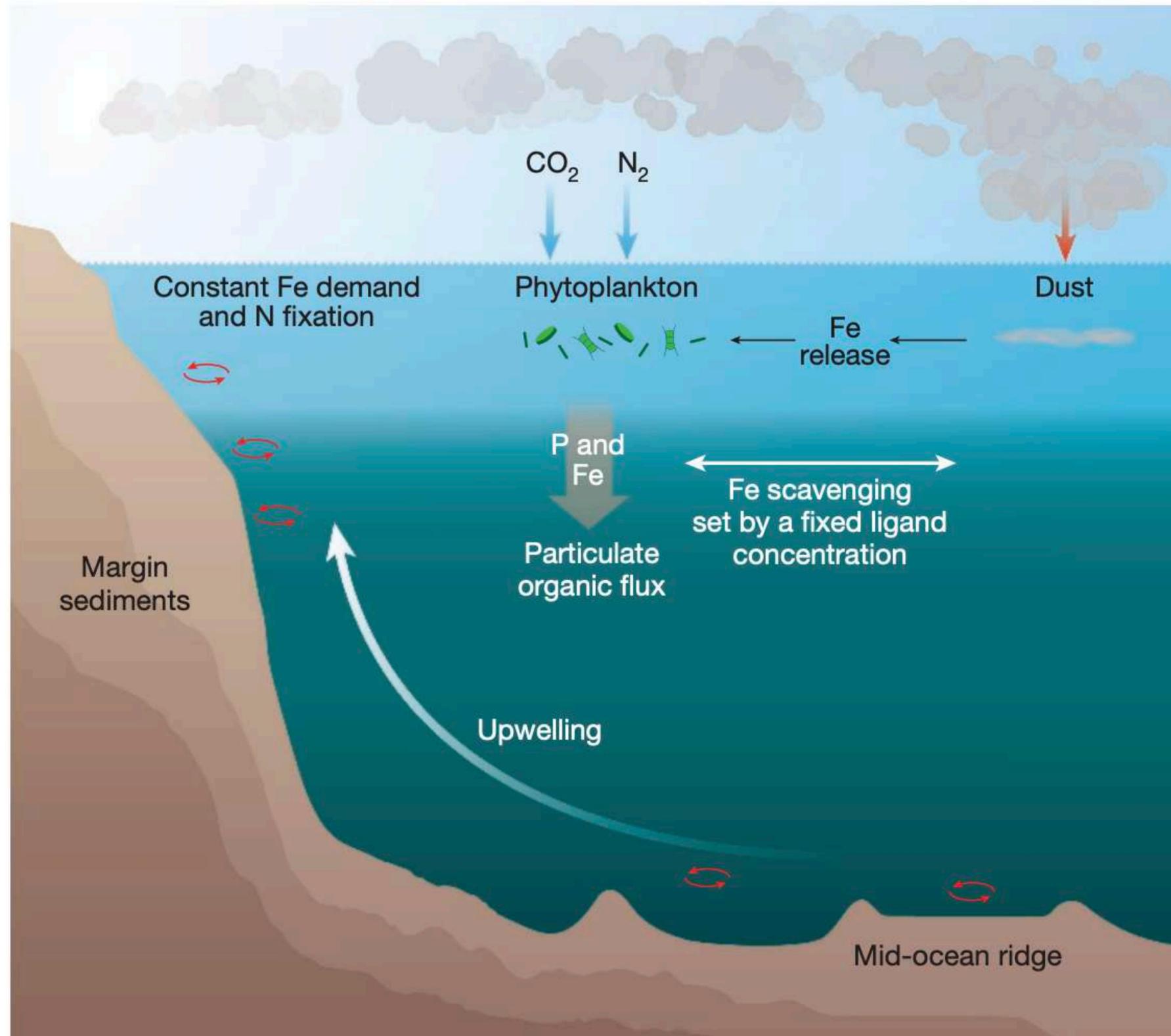
Tagliabue et al., 2019

# Fe cycle

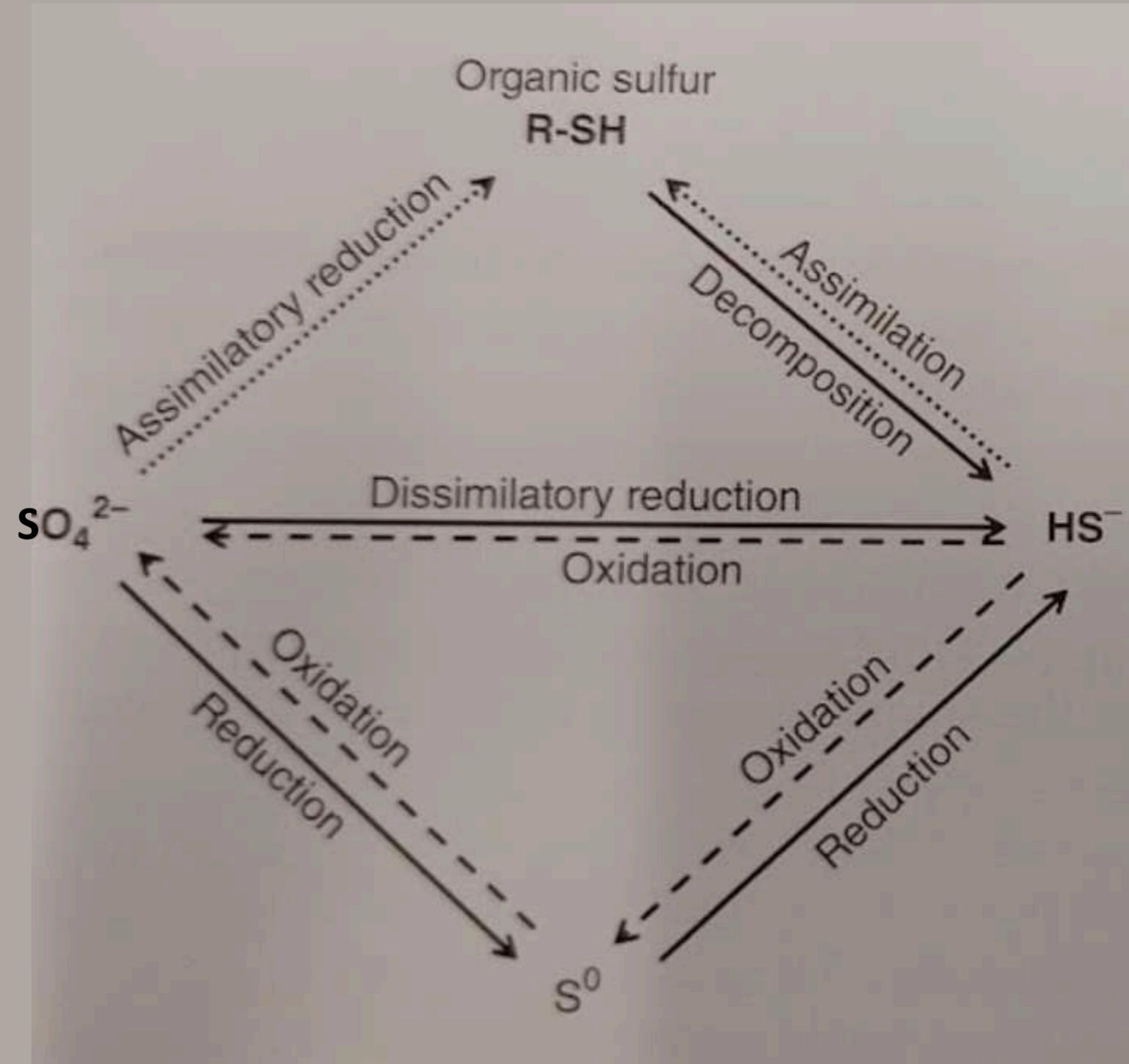
The major external **source is dust**, with the iron supplied from **continental margins and hydrothermal activity** on mid-ocean ridges thought to be lost from the dissolved pool close to the source

Release of **iron from dust or supply of iron from upwelling stimulates biological activity, nitrogen fixation and particulate organic matter fluxes** in a constant relationship to major nutrients (that is, they are biogeochemically coupled)

**In the ocean interior, iron regeneration and scavenging is controlled by fixed concentrations of iron-binding organic ligands**



# Sulfur



# Sulfur

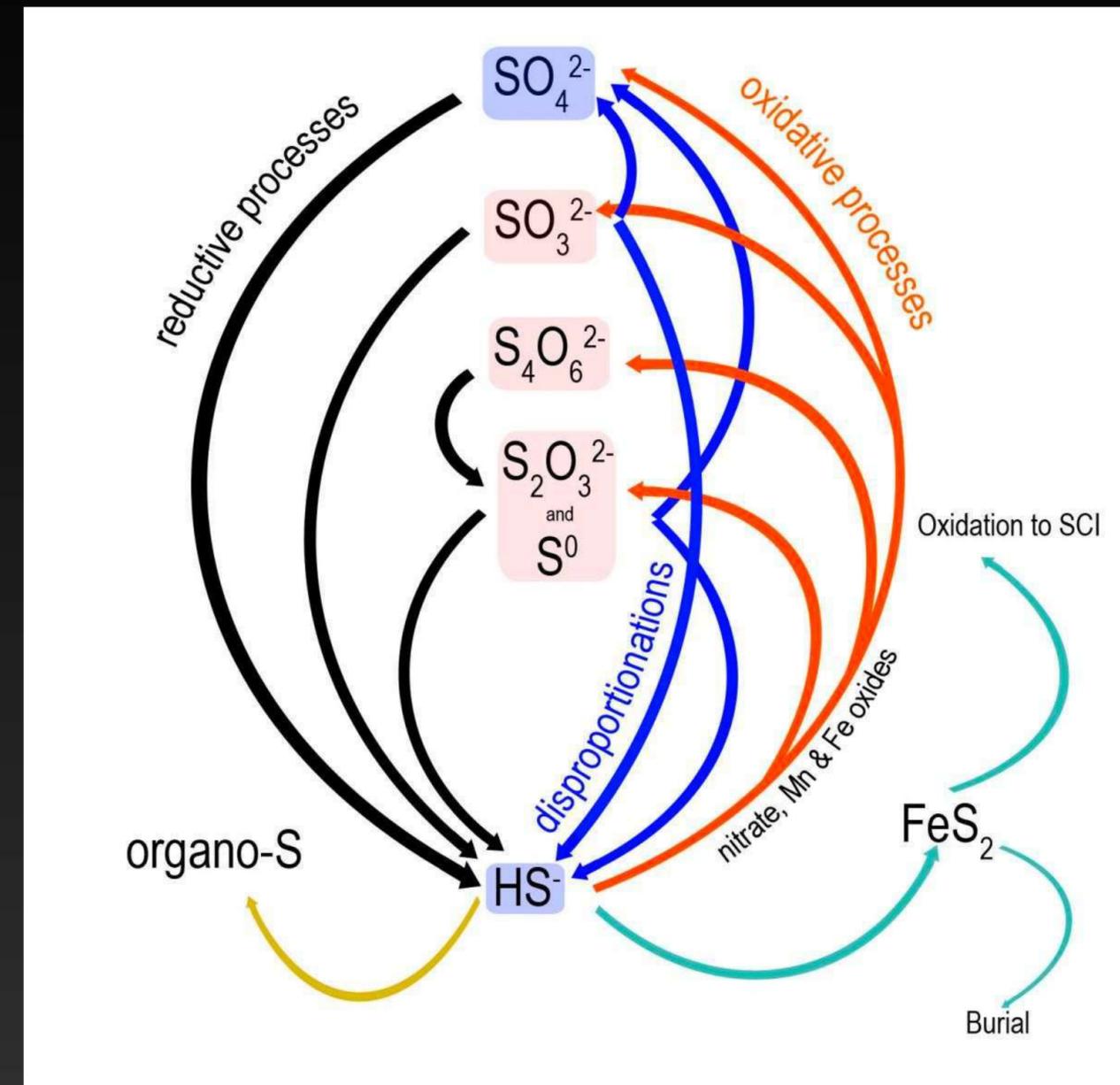
1% cellular mass  
Proteins  
Sulfolipids

Different oxidation states:

-2 (sulfhydryl, sulfide) 0  
(sulfur elemental)

+6 (sulfate)

Ocean largest reservoir of  $\text{SO}_4^{2-}$



<https://www.microbial-ecology.net/research/missing-links-in-the-marine-sulfur-cycle-identity-and-functions-of-microorganisms-utilizing-sulfur-cycle-intermediates-and-organic-sulfur-molecules-in-marine-sediments>

# Focus on S metabolisms

## \* Sulfur Oxidizing Bacteria (SOB):

- ❖ Strict aerobes, use  $H_2S$
- ❖ Hydrothermal vents, cold seeps, symbionts with invertebrates
- ❖ Some are autotrophs
- ❖ Production of sulfate,  $SO_4^{2-}$

## \* Sulfate Reducing Bacteria (SRB):

- ❖ Important for organic matter degradation, nitrate-rich waters
- ❖ Production of  $H_2S$  PRODUCTION, TOXIC
- ❖  $H_2S$  is substrate for SOB (Sulfur oxidizing bacteria) and consortia with anaerobic oxidation of methane by Archaea, compete with SBR (Sulfate reducing bacteria) for acetate,  $H_2$  and use of  $SO_4^{2-}$
- ❖ Consortium with Archaea that do anaerobic oxidation of methane (AOM, ANME)

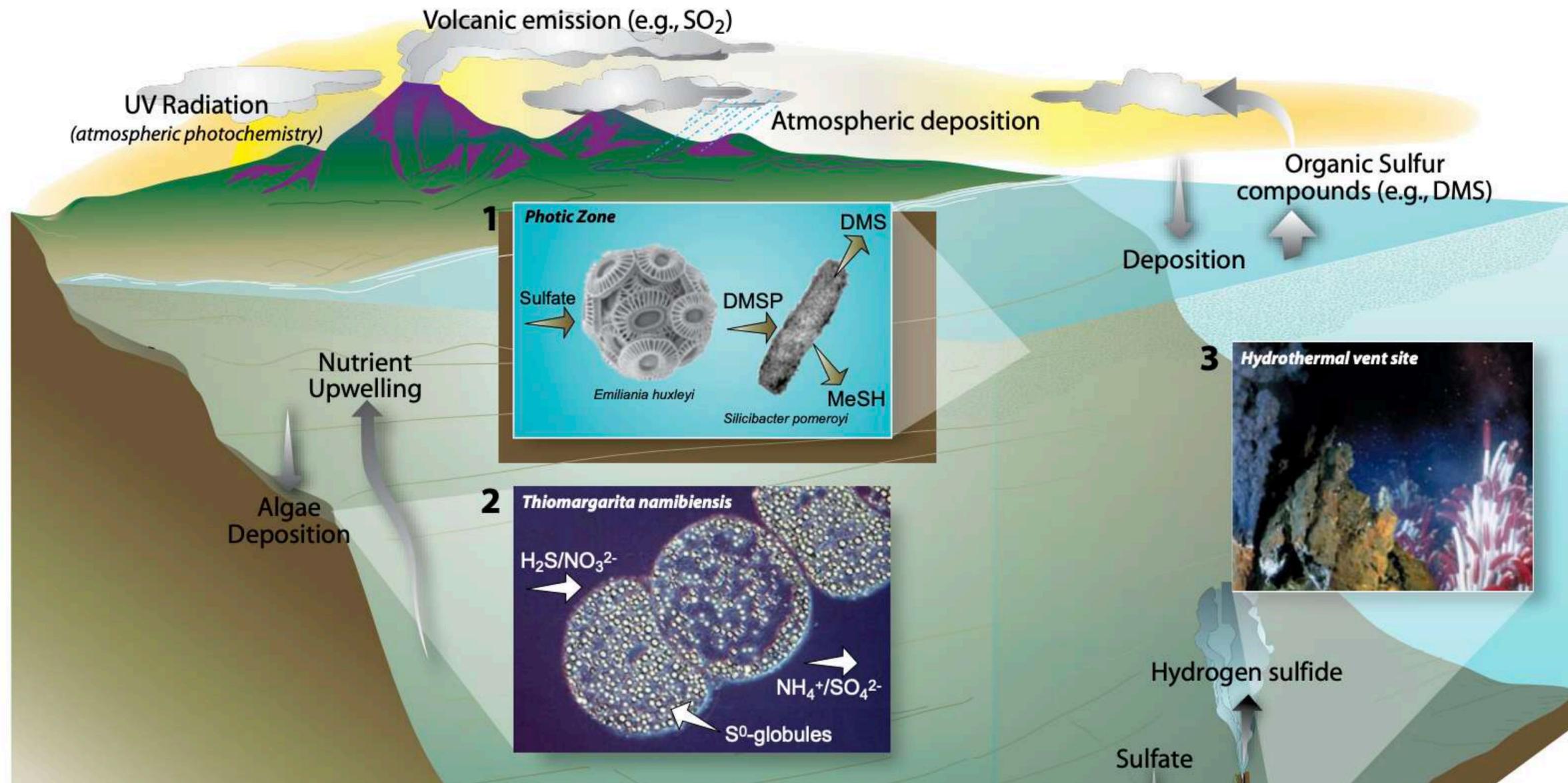
## • Anaerobic oxidation of methane by consortia: methanotrophic Archaea (AMNE) and SRB

- Oxidic anoxic interface
- Utilisation of  $CH_4$  and  $SO_4^{2-}$
- Production of bicarbonate and  $HS^-$  (sulfide) → reef construction at seeps
- Early metabolism Earth

- Methanogenesis: Euryarchaeota uses  $H_2$  and  $CO_2$  to produce  $CH_4$  for biomass:  
★methanogens, living with fermenters and compete with SBR

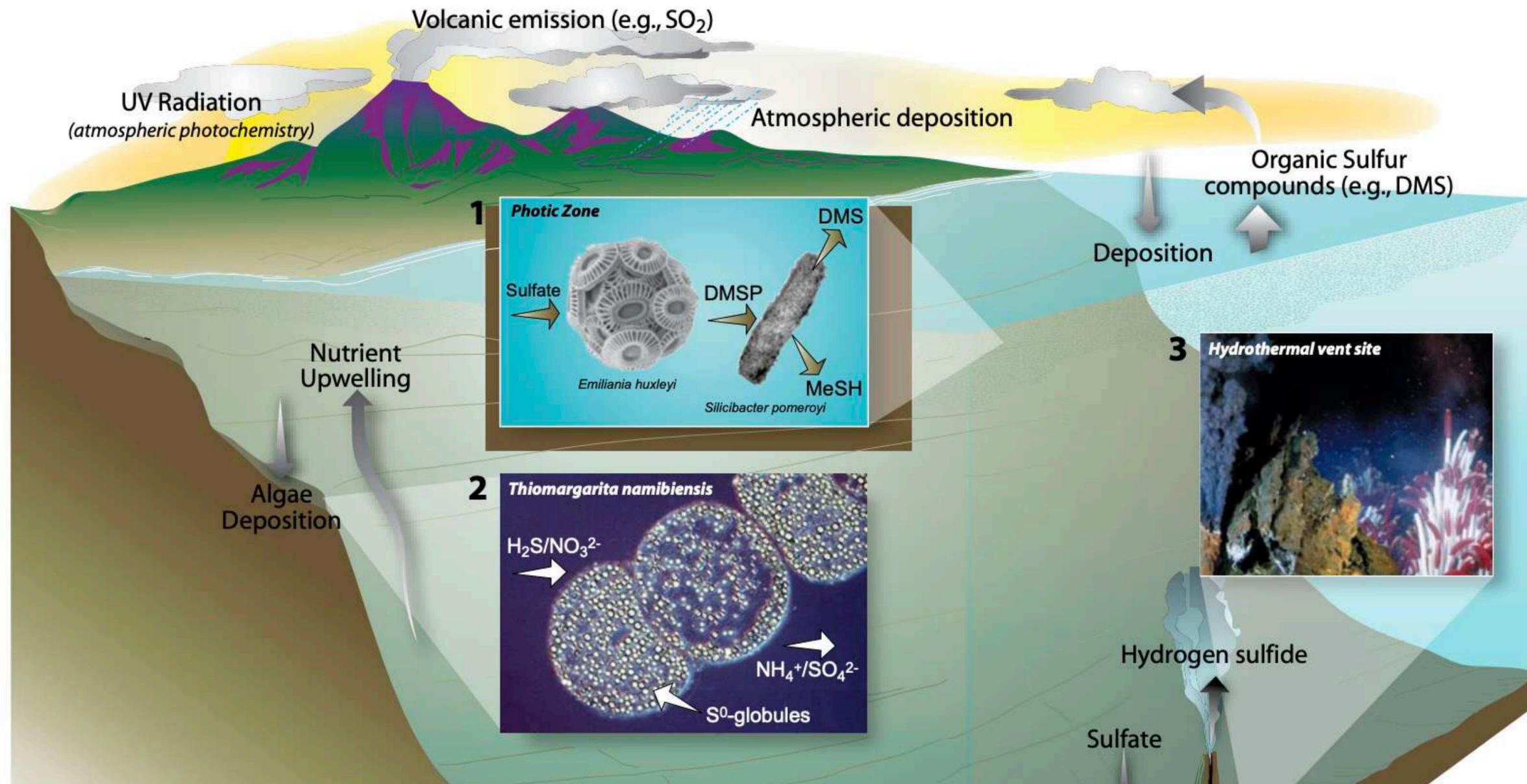
# Sulfur

- Dissimilative sulfate reduction: energy generation, production of  $H_2S$  by sulfate reducing bacteria, in anaerobic sediment
- Assimilative sulfate reduction: using ATP  $\rightarrow$  into biomass
- DMSP, dimethylsulphoniopropionate produced from some dinoflagellates and prymnesiophytes



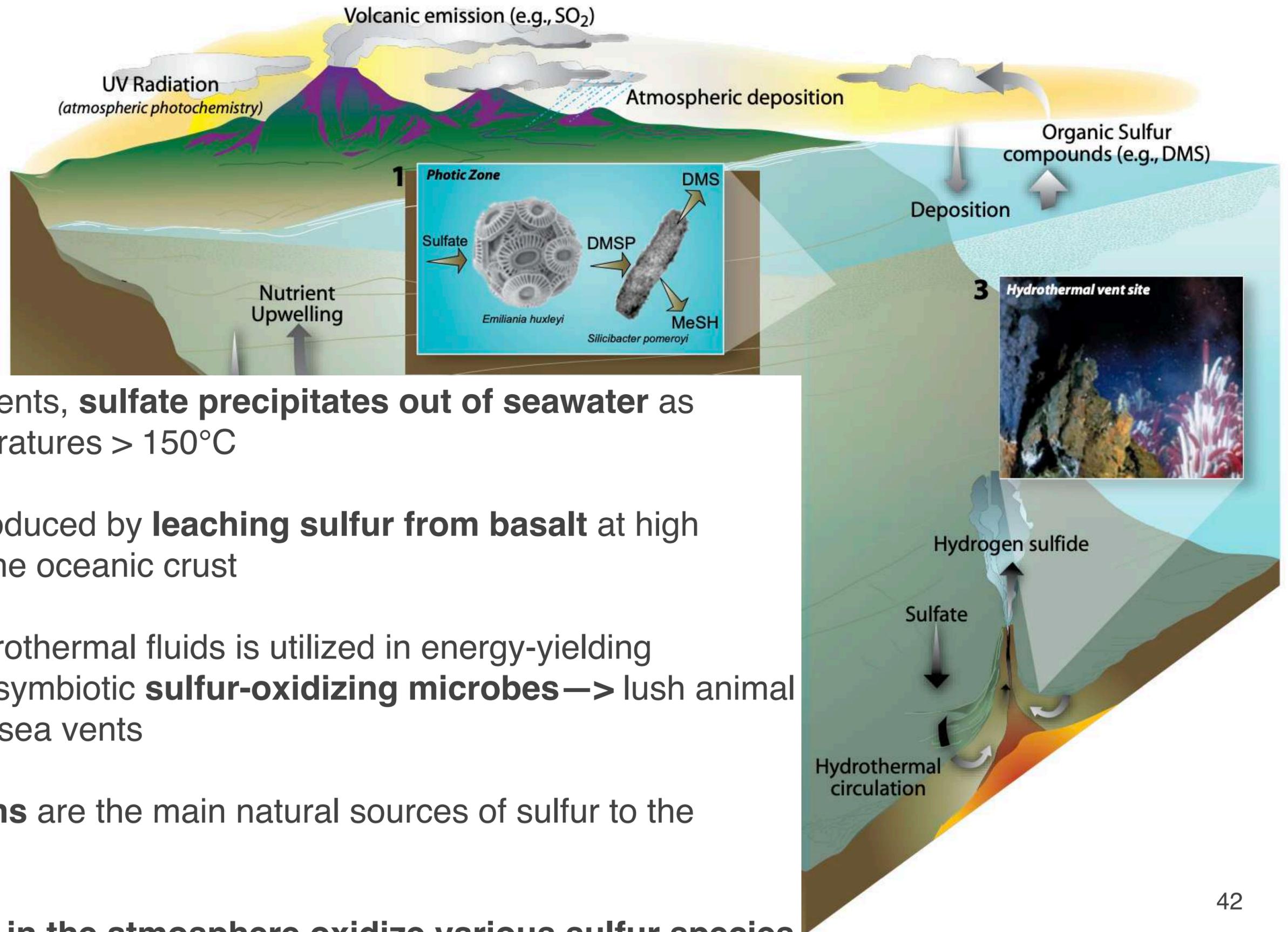
In the upper water column, metabolism of organic sulfur compounds is of particular relevance

Dimethylsulfoniopropionate (DMSP) produced by algae (e.g., *Emiliana huxleyi*) is utilized by a diverse assemblage of microbes (e.g., *Silicibacter pomeroyi*), leading either to the production of methanethiol (MeSH) or dimethylsulfide (DMS), both of which are highly reactive volatile compounds that can escape to the atmosphere



On the continental shelf, sulfate reduction contributes significantly to organic-matter degradation. The hydrogen sulfide produced can be re-oxidized by so-called colorless sulfur-oxidizing bacteria (e.g., *Thiomargarita namibiensis*).

These processes are important in coastal upwelling regions, such as off the coast of Namibia, where *Thiomargarita namibiensis* becomes abundant. It is also in these regions that large sedimentary deposits of phosphorites are found.



At deep-sea hydrothermal vents, **sulfate precipitates out of seawater** as anhydrite (CaSO<sub>4</sub>) at temperatures > 150°C

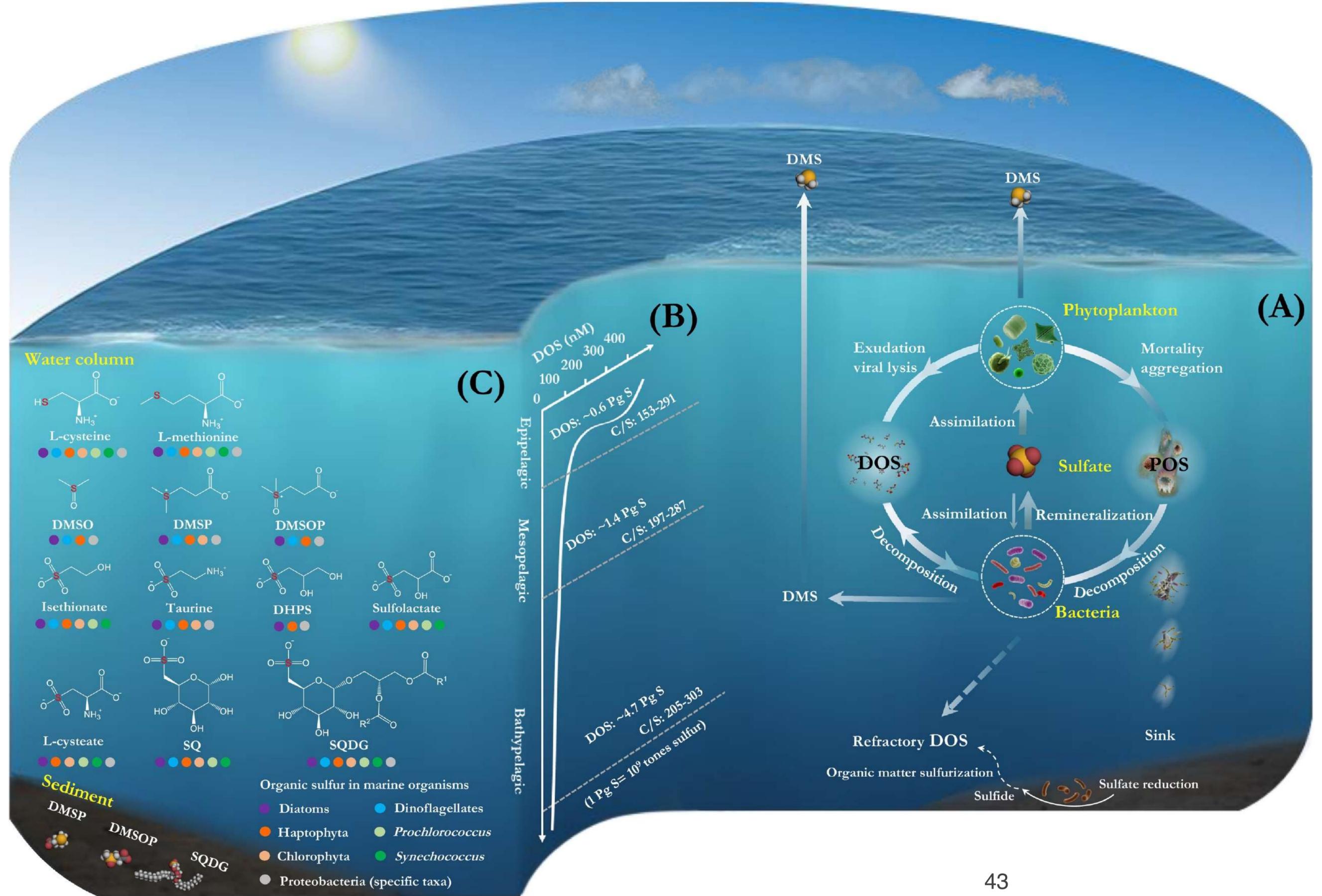
Hydrogen sulfide, **H<sub>2</sub>S** is produced by **leaching sulfur from basalt** at high temperatures (~ 400°C) in the oceanic crust

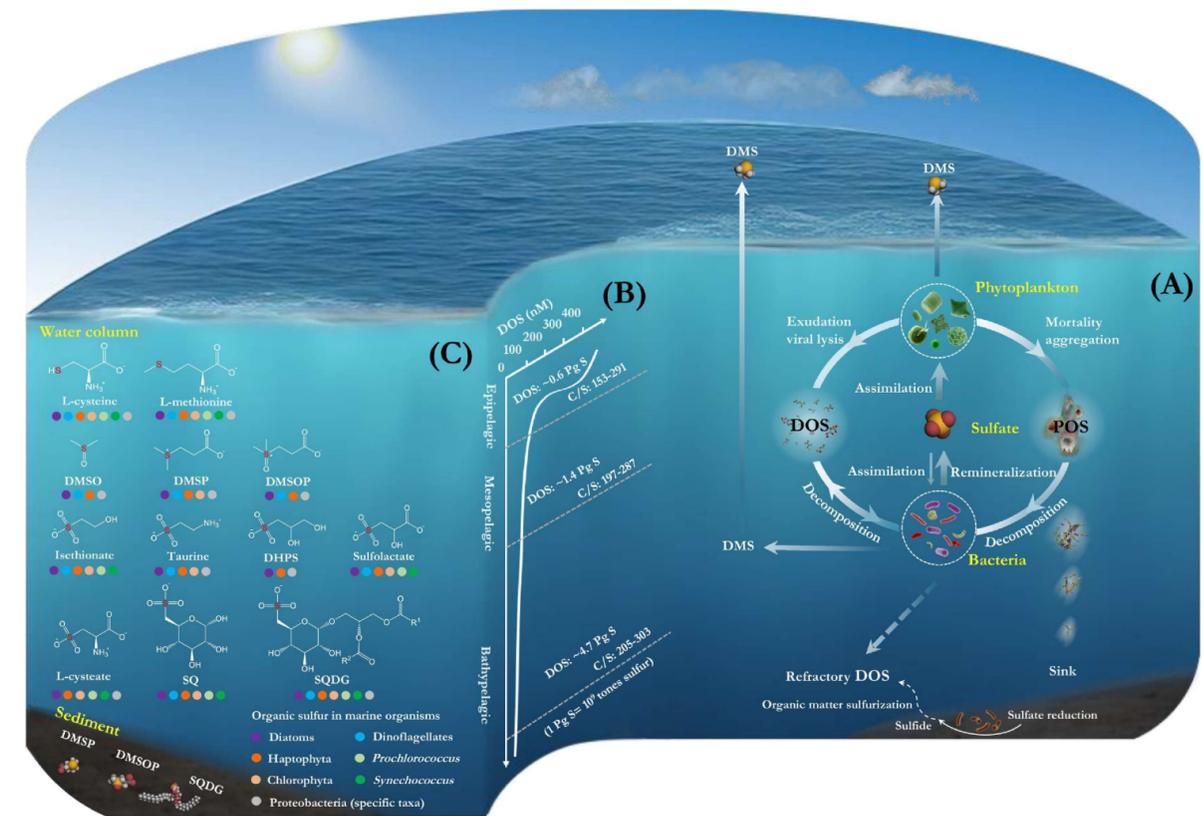
**H<sub>2</sub>S** present in reduced hydrothermal fluids is utilized in energy-yielding reactions by free-living and symbiotic **sulfur-oxidizing microbes** → lush animal communities found at deep-sea vents

On land, **volcanic emissions** are the main natural sources of sulfur to the atmosphere

**Photochemical processes in the atmosphere oxidize various sulfur species**

# The organic sulfur cycle



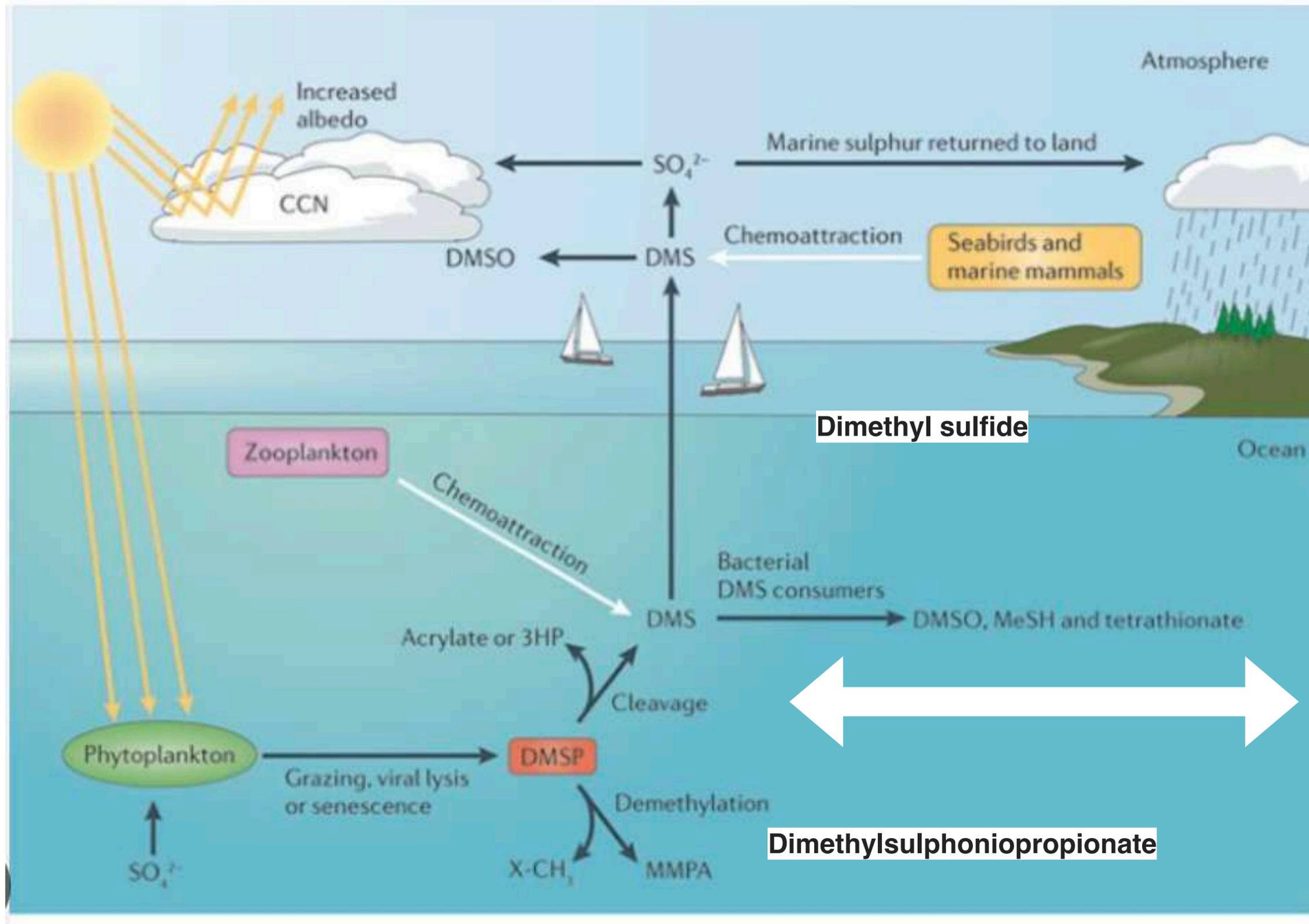


Trends in Microbiology

Tang & Liu, 2023

Dissolved organic sulfur (DOS) concentrations and an estimation of DOS stock in the oceanic water column

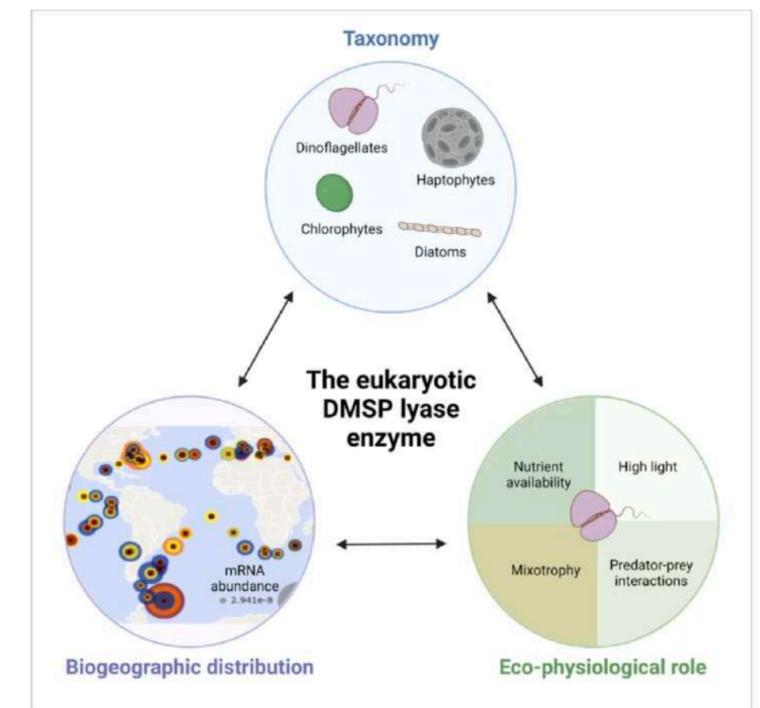
Natural organosulfur compounds and their producers in the ocean. Abbreviations: DHPS, 2,3-dihydroxypropane-1-sulfonate; DMS, dimethylsulfide; DMSO, dimethylsulfoxide; DMSOP, dimethylsulfoxonium propionate; DMSP, dimethylsulfoniopropionate; POS, particulate organic sulfur; SQ, sulfoquinovose; SQDG; sulfoquinovosyldiacylglycerol.



Curson et al., 2011

**DSMP → DMS**

**And MICROBES (BACTERIA TOO)**



Shemi et al., 2023

DMSP—> DMS, dimethyl sulfide

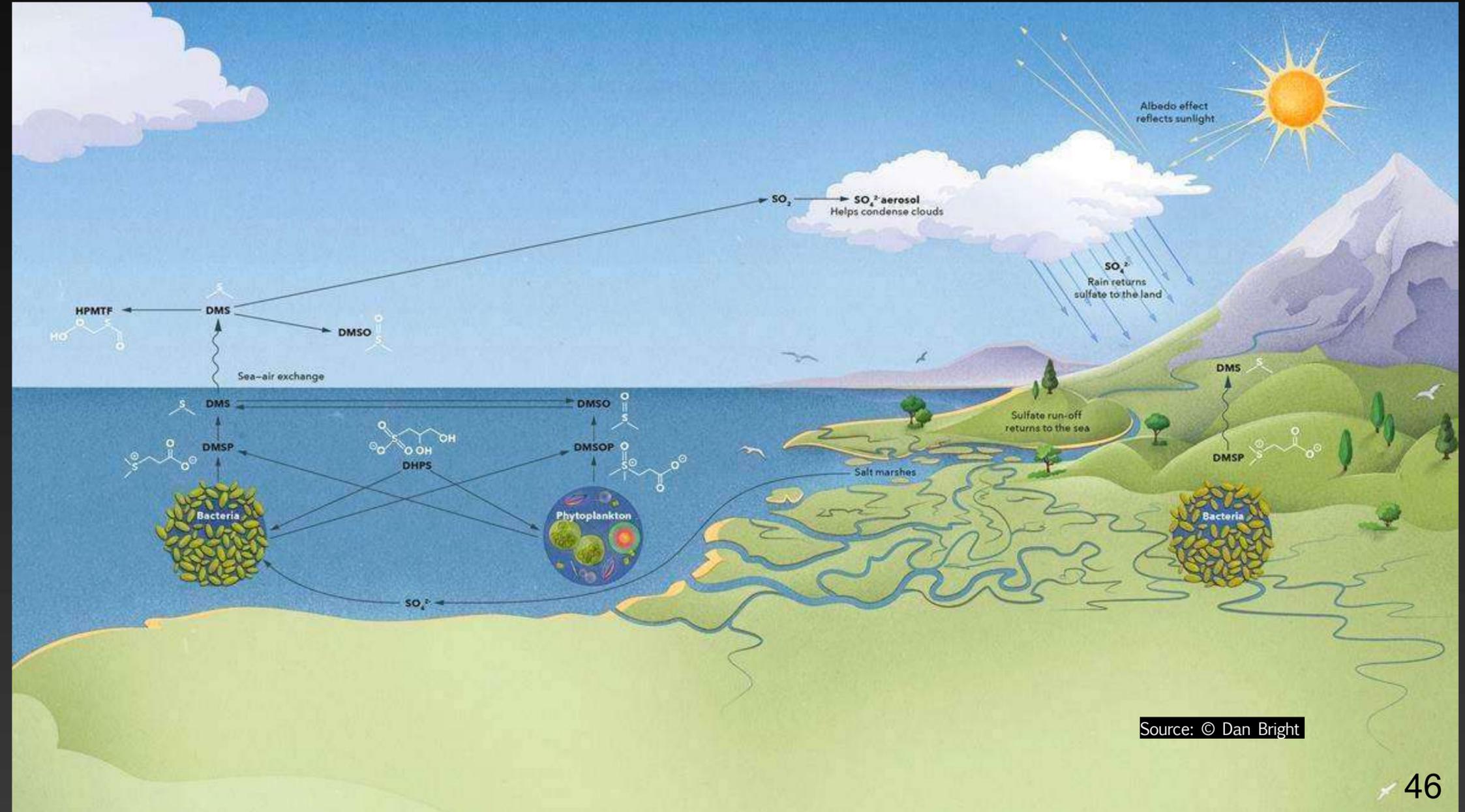
DMS is a gas, ~21 Gt y<sup>-1</sup>, once it is photooxidized acts as CCN

DMS acts as osmotic stress- and cryo-protectant, antioxidant, defensive functions

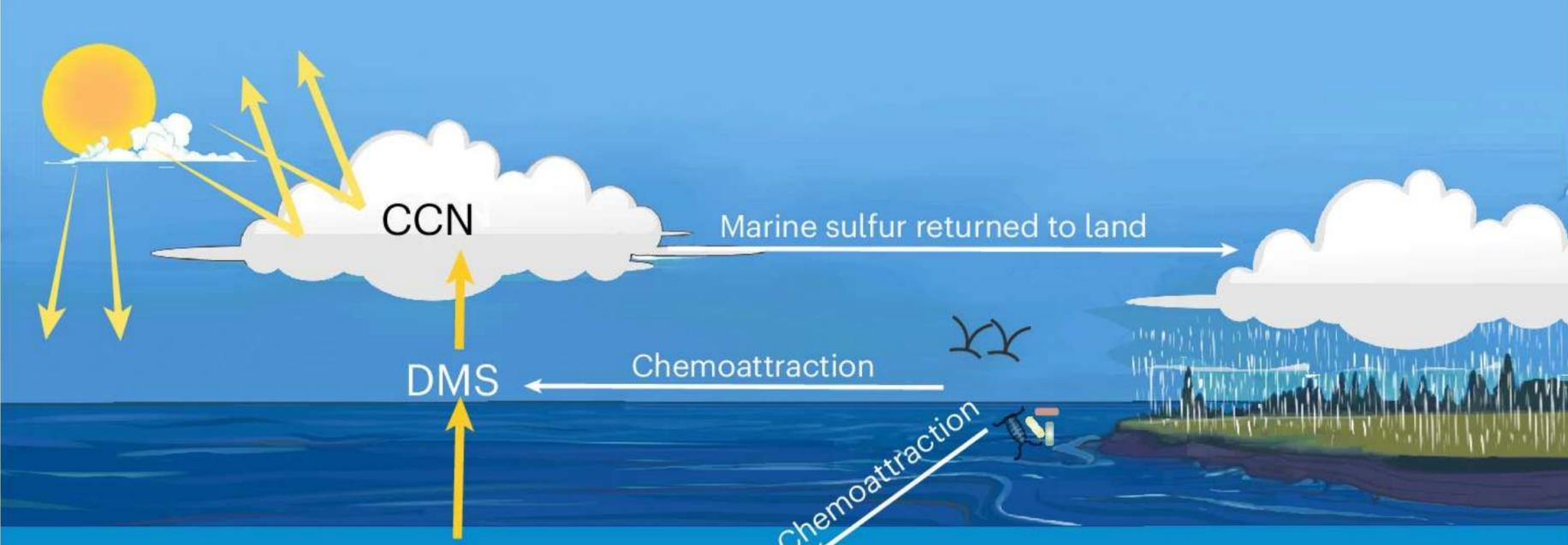
Balancing growth by  
recreating reduced sulfur  
and reducing power

Released by healthy  
phytoplankton and during  
copepod grazing

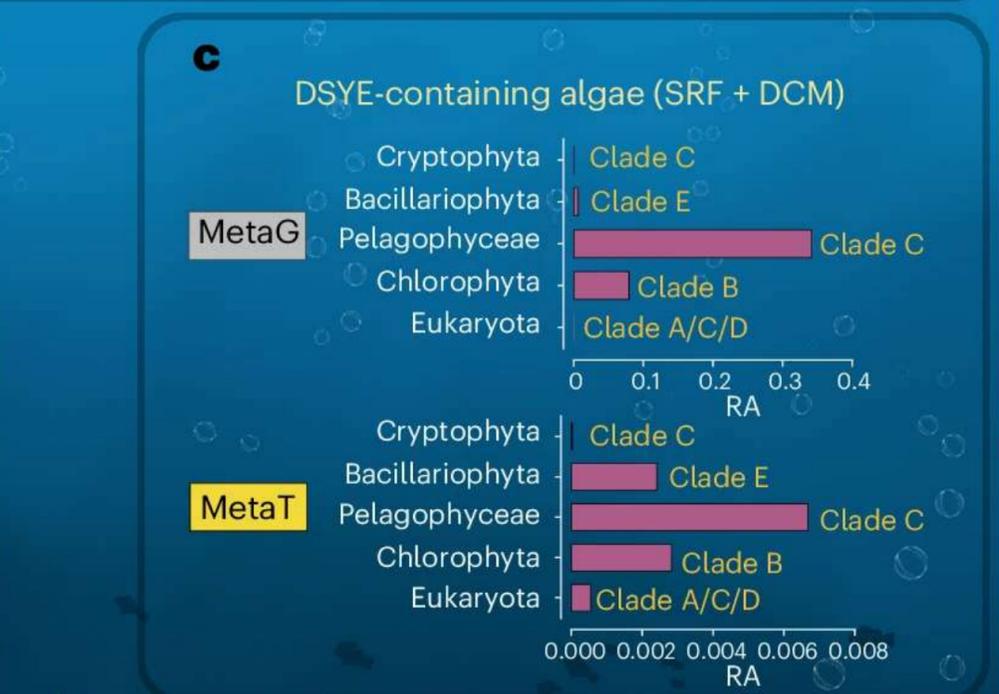
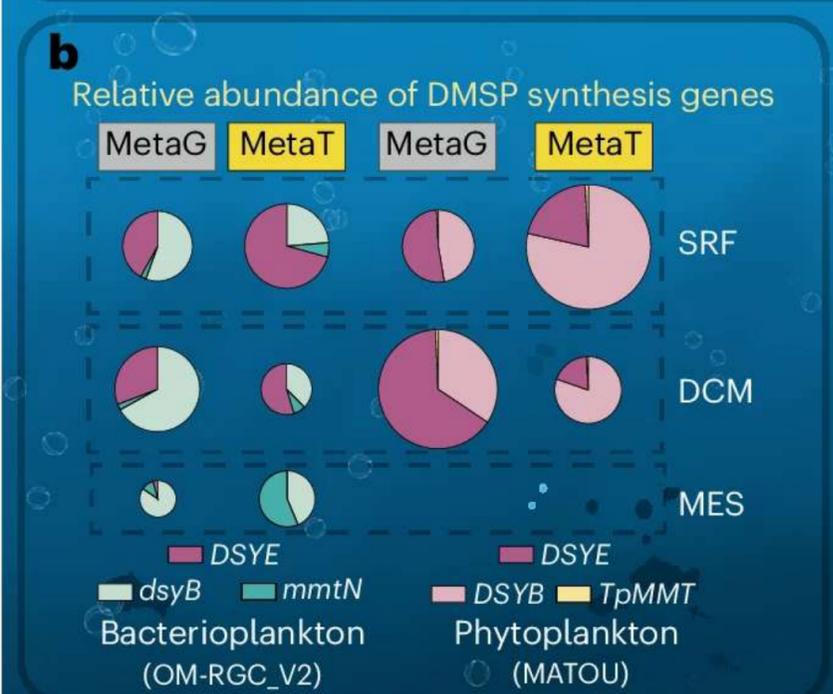
Bacteria act w. different  
enzyme to acquire S



# Overview of key DMSP biosynthesis enzymes and pathways and their environmental importance



Dimethylsulfoniopropionate (DMSP) is an abundant marine organosulfur compound with roles in stress protection, chemotaxis, nutrient and sulfur cycling and climate regulation

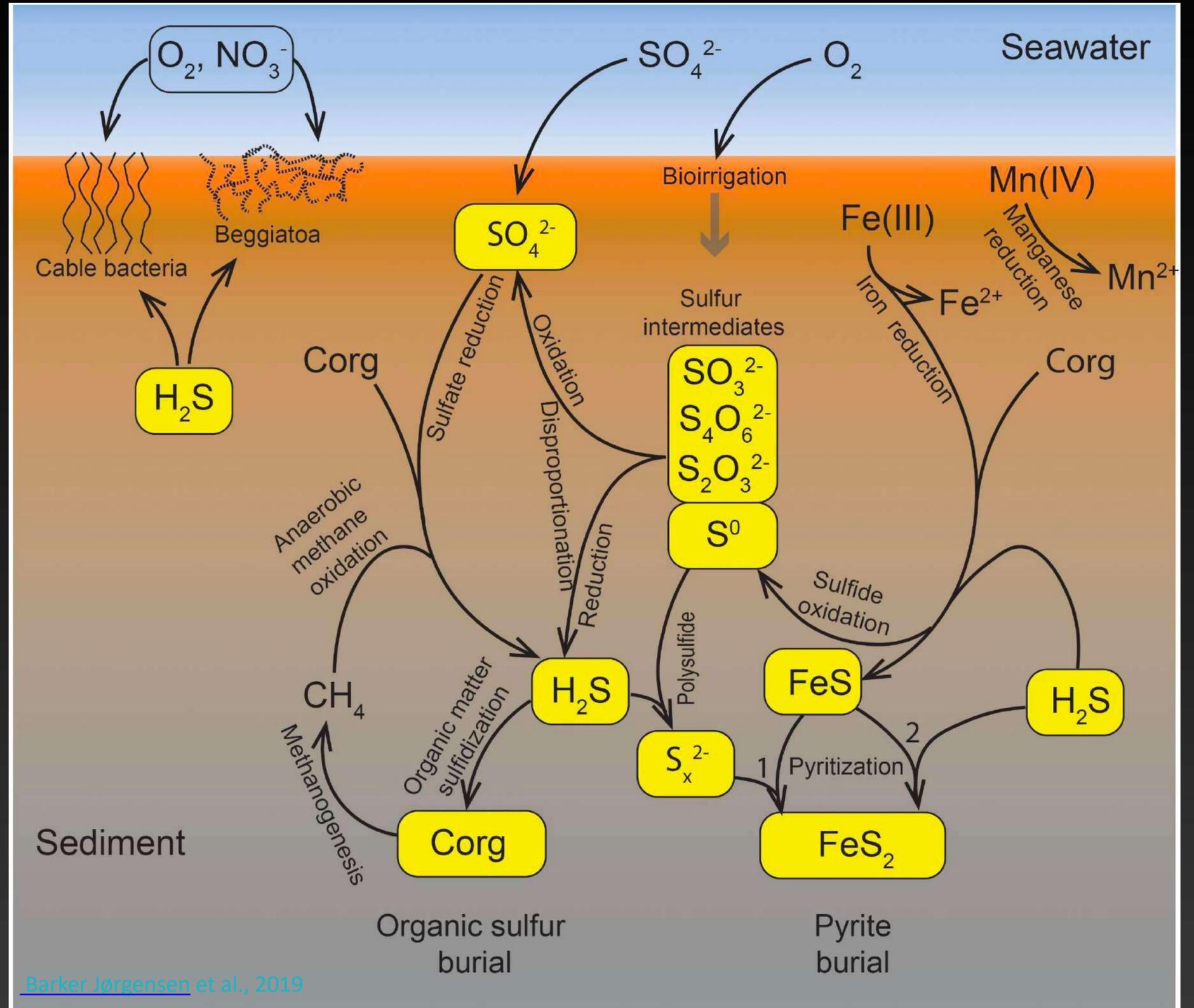


Key DMSP synthesis and cleavage pathways are indicated with known algal and bacterial S-methyltransferases

CCN, cloud condensation nuclei. MetaG, metagenomes data; MetaT, metatranscriptomes data; RA, relative abundance. SMM, S-methylmethionin

# Sulfur IV

- S is connected with Fe, Mn, C (CH<sub>4</sub>)
- Organic matter degradation
- Biochemical sediment donation due to anaerobic metabolisms



# Silicon I

- Earth crust, sea floor and rock weathering and hydrothermal vent inputs
- Dissolution of silicate at alkaline pH (microbes degrade dead diatom OM and expose silicate to sw)
- Diatoms, radiolarians, flagellates, Cyanobacteria in mats, sponges and gorgonian corals
- Limiting element for diatoms, Si:N is 1:4
- Diatom bloom sequester ~ 40% organic carbon (~1.5-2.8 Gt y<sup>-1</sup>)
- Human inland structuring actions reduce dissolved silicate flux to ocean —> favouring non-siliceous plankton bloom —> flagellate bloom —> less nutritional values and less productive fishery and HAB (harmful algal bloom)

# Silicon II

Input, output, and biological silicon fluxes, with possible balance

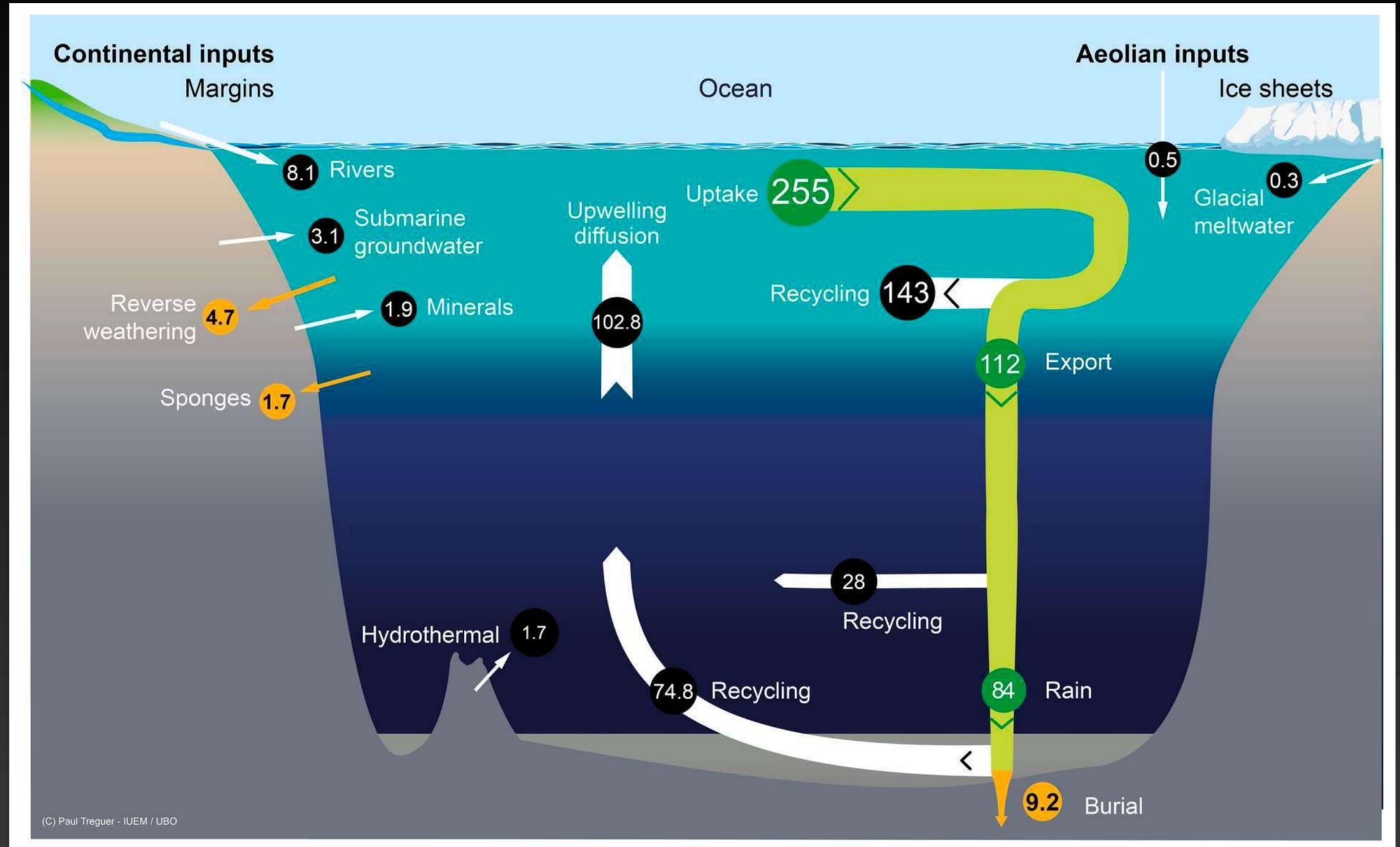
Total silicon inputs = total silicon outputs = 15.6 Tmol Si yr<sup>-1</sup> in reasonable agreement with the individual range of each flux (F)

White arrows represent fluxes of net sources of dissolved silicic acid (dSi) and/or of dissolvable amorphous silica (aSi) and of dSi recycled fluxes

Orange arrows represent sink fluxes of silicon, either as biogenic silica or as authigenic silica

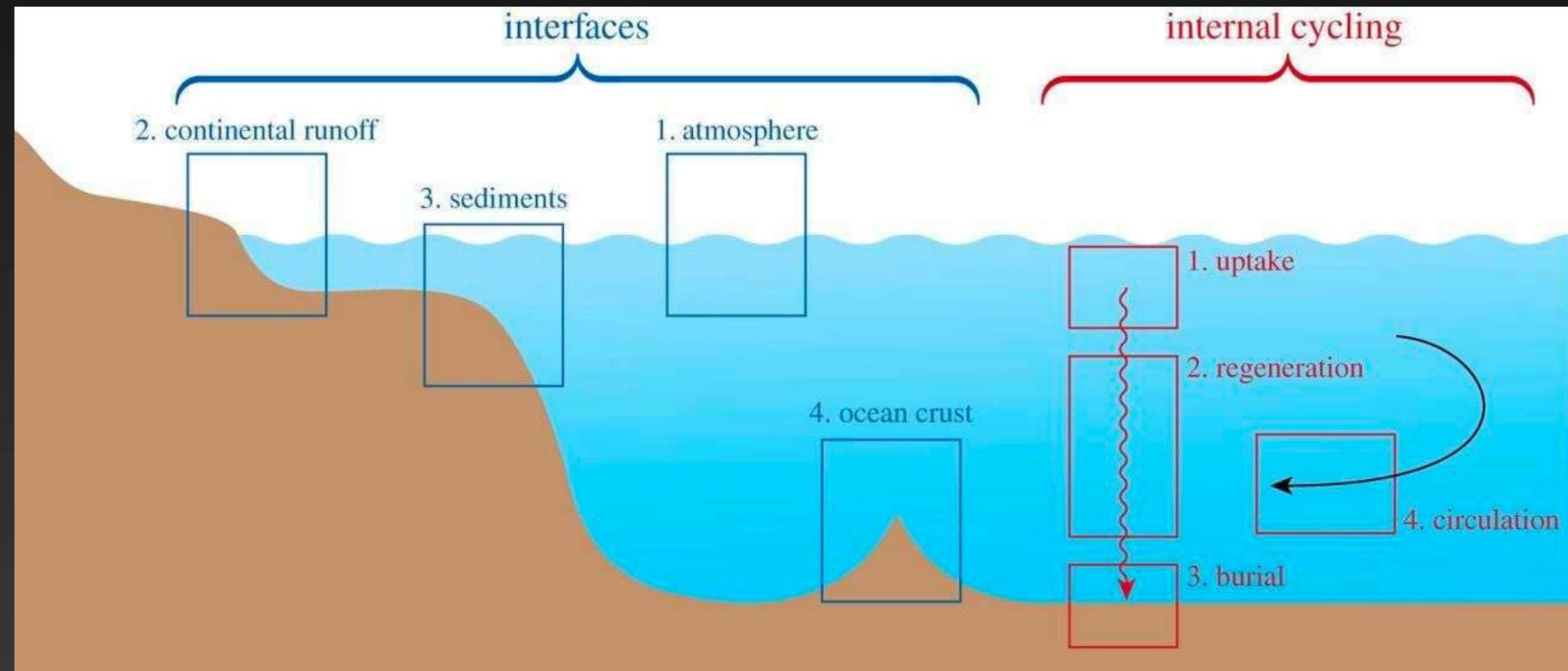
Green arrows correspond to biological (pelagic) fluxes

Fluxes in teramoles of silicon per year



# Trace Metal I

- 82 naturally occurring elements, and all are found dissolved in seawater, sometimes at extremely low concentration
- Important in enzymes functioning and protein structure—> LIFE



Ocean boundaries or interfaces at which trace elements can enter or be removed from seawater, and the major processes involved in internal cycling of trace elements in seawater. (Adapted from the GEOTRACES Science Plan, ISSN 1932-7951)

# Trace Metal II

- Limited solubility
- Removal processes

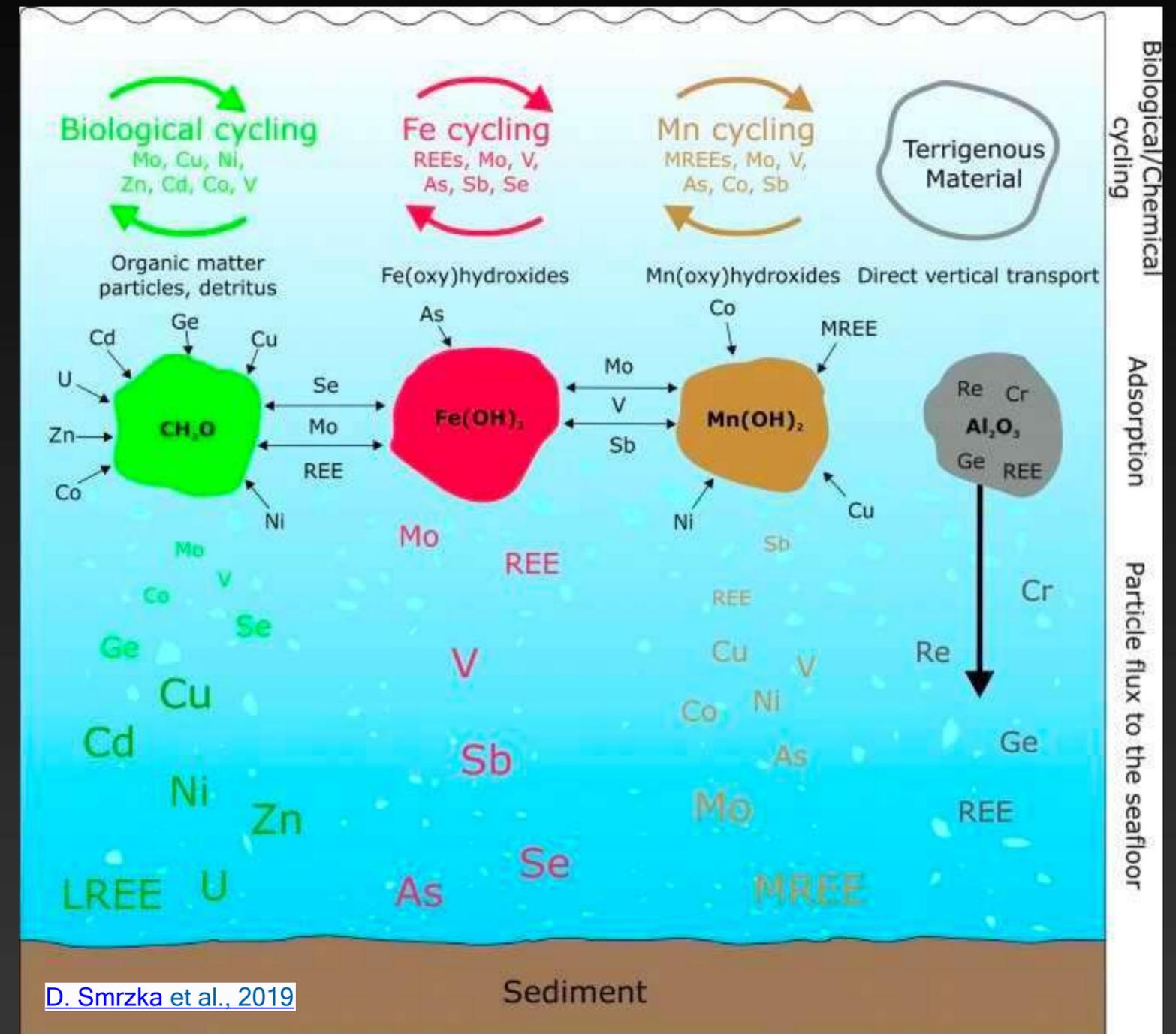
Four solid phases involved in cycling and vertical transport are considered: organic matter (green), iron (oxy)hydroxides (red), manganese (oxy)hydroxides (orange), and terrigenous material (brown)

Elements are cycled in the photic zone biologically by planktonic organisms and chemically by hydroxide phases, after which trace elements are adsorbed to these phases and transported to the seafloor as particle rain

Terrigenous phases are not involved in surface water cycling

Although all elements may adsorb to all solids, the focus here is on the most relevant ones for the respective phases

The size of the font of element symbols denotes the importance of organic matter, iron and manganese oxides, and terrigenous particles as a shuttle for the respective element from the photic zone to the seafloor.

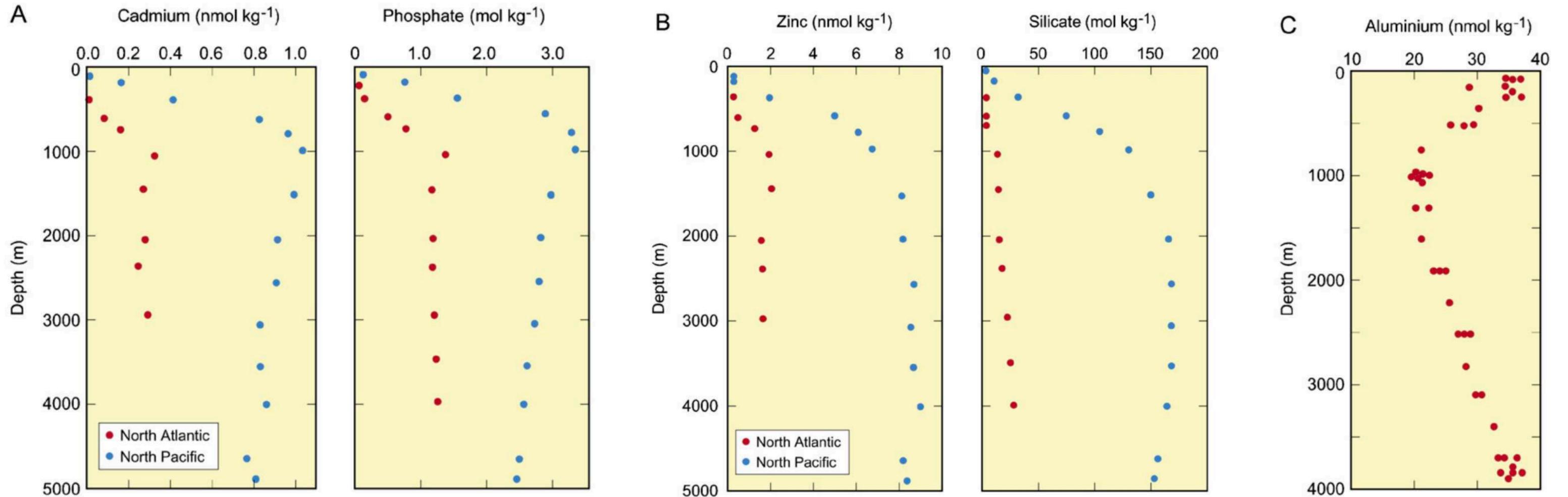


**Table 1.** Important biogeochemical processes in the ocean and the trace metals thought to be fundamental to their action

Biogeochemical process	Important trace elements
Carbon fixation	Fe, Mn
CO <sub>2</sub> concentration/acquisition	Zn, Cd, Co
Silica uptake – large diatoms	Zn, Cd, Se
Calcifiers – coccolithophores	Co, Zn
N <sub>2</sub> fixation	Fe, Mo (?V)
Denitrification	Cu, Fe, Mo
Nitrification	Cu, Fe, Mo
Methane oxidation	Cu
Remineralisation pathways	Zn, Fe
Organic N utilisation	Fe, Cu, Ni
Organic P utilisation	Zn
Formation of volatile species	Fe, Cu, V
Synthesis of photopigments	Fe and others
Toxicity	Cu, As (?Cd, Pb)

Derived from Morel et al. (2003) and Morel and Price (2003), and references therein.

# Trace element depth profiles



GEOTRACES – An international study of the global marine biogeochemical cycles of trace elements and their isotopes SCOR Working Group1 Received 28 April 2006; accepted 19 September 2006

**Table 1** Overview of trace element properties, behavior, and distribution in seawater

Element	Main source to the ocean	Essential nutrient	Dissolved concentration in nmol per kg seawater	Speciation in seawater and oxidation state	Vertical distribution	Water column cycling and transport
Mo	Rivers	Yes	111.5 <sup>a</sup>	MoO <sub>4</sub> <sup>2-</sup> /Mo(VI)	Conservative	Fe- and Mn-oxides
U	Rivers	No	13.8 <sup>b</sup>	UO <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub> <sup>4-</sup> /U(VI)	Conservative	Organic matter
Cd	Rivers	No	0.0014–1.1 <sup>c</sup>	CdCl <sup>+</sup> /Cd(II)	Nutrient-like	Organic matter
Ni	Rivers	Yes	2.1–11 <sup>c</sup>	Ni <sup>2+</sup> /Ni(II)	Nutrient-like	Organic matter
Cu	Rivers, atmosphere, hydrothermal vents	Yes	0.5–5 <sup>c</sup>	CuCO <sub>3</sub> /Cu(II)	Nutrient-like	Organic matter
Zn	Rivers, hydrothermal vents	Yes	0.07–9 <sup>c</sup>	Zn <sup>2+</sup> /Zn(II)	Nutrient-like	Organic matter
Re	Rivers	No	0.02–0.09 <sup>d</sup>	ReO <sub>4</sub> <sup>2-</sup> /Re(II)	Conservative	None
V	Rivers	Yes	29.8–37.4 <sup>e</sup> , 27.4–33.4 <sup>f</sup>	VO <sub>2</sub> (OH) <sub>3</sub> <sup>2-</sup> , H <sub>2</sub> VO <sub>4</sub> <sup>-</sup> /V(V)	Nutrient-like	Fe- and Mn-oxides
Co	Atmosphere	Yes	0.016–0.118 <sup>g</sup> , 0.025–0.1 <sup>h</sup>	Co <sup>2+</sup> /Co(II)	Scavenged	Mn oxides and organic matter
Cr	Rivers	No	8.1–9.4 <sup>i</sup> , 0.5–5 <sup>j</sup>	CrO <sub>4</sub> <sup>2-</sup> /Cr(VI)	Nutrient-like	Terrigenous particles
As	Rivers, hydrothermal vents	No	13.3–24 <sup>k</sup> , 15–20 <sup>l</sup>	HAsO <sub>4</sub> <sup>2-</sup> /As(V)	Nutrient-like	Fe- and Mn-oxides
Sb	Rivers	No	0.8–1.1 <sup>l</sup> , 1.4–2.05 <sup>m</sup>	Sb(OH) <sub>6</sub> <sup>-</sup> /Sb(V)	Conservative	Fe oxides
Se	Rivers	No	0.76–2.5 <sup>n</sup> , 0.4–1.6 <sup>o</sup>	SeO <sub>4</sub> <sup>2-</sup> , SeO <sub>3</sub> <sup>2-</sup> /Se(VI), Se(IV)	Nutrient-like	Fe oxides
Ge	Rivers	No	0.007–0.115 <sup>p</sup>	Ge(OH) <sub>4</sub>	Nutrient-like	Organic matter and terrigenous particles
REEs	Rivers and atmosphere	No	0.0073–0.039 (La) <sup>q</sup> , 0.0003–0.0015 (Lu) <sup>q</sup> , 0.07–0.23 (Y) <sup>q</sup> , 0.113–0.210 (Y) <sup>r</sup>	[REE]CO <sub>3</sub> <sup>+</sup> , [REE](CO <sub>3</sub> ) <sub>2</sub> <sup>2-</sup> /REE(III), except Ce(III) and Ce(IV)	Nutrient-like except Ce (Scavenged)	Organic matter (LREEs), Fe and Mn-oxides (MREEs), and terrigenous particles

- Anthropogenic activities
- Microbes as acting force in mobilisation or sequestration
- Biomagnification and bioaccumulation of metals
- Different states

