

L04: Microbes in Ocean Processes

L04a: Biogeochemical Carbon Cycle

Healthy Ocean ↔ Functioning Ocean

Functioning Ocean ↔ Functioning C biogeochemical cycle

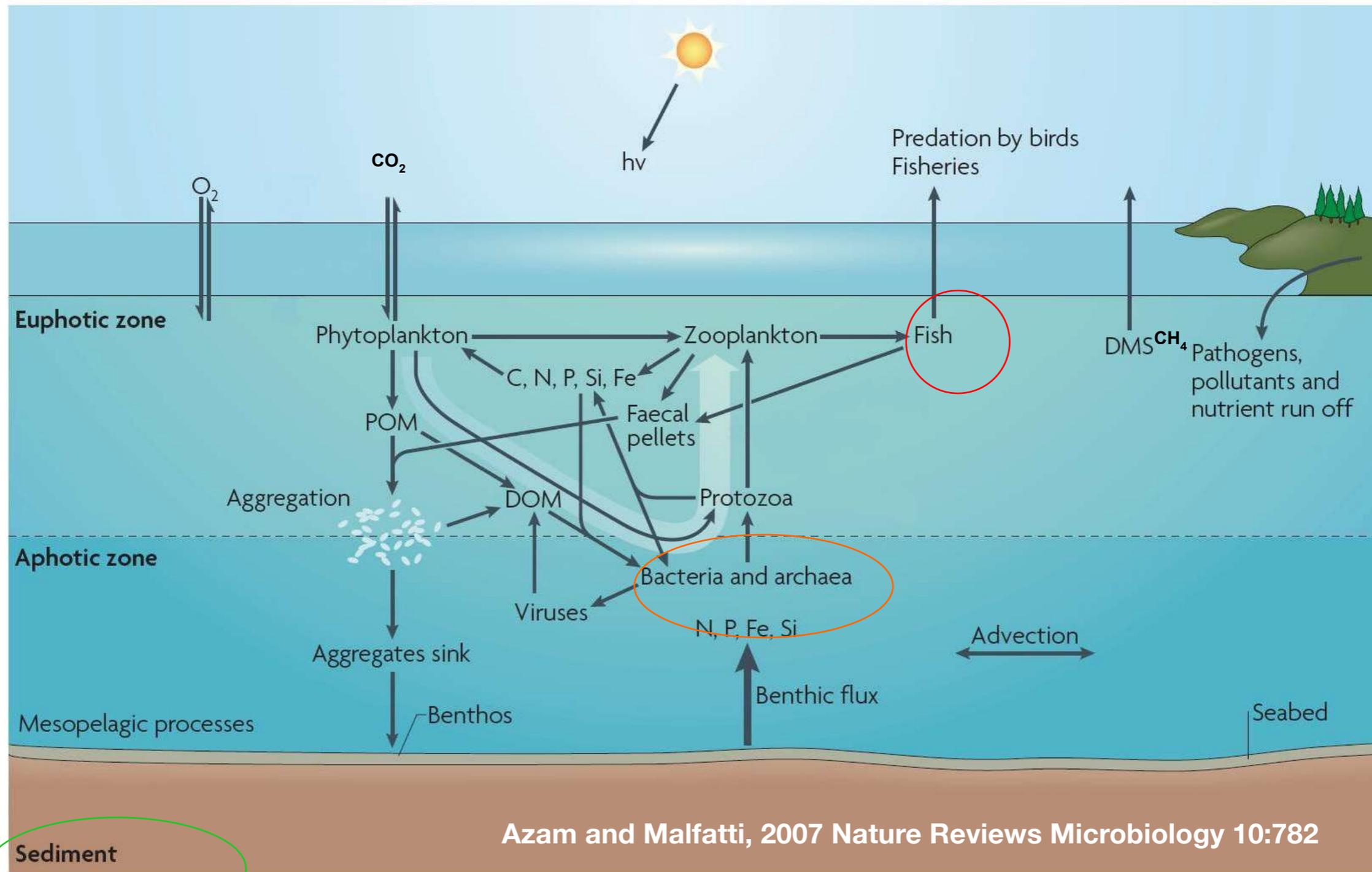
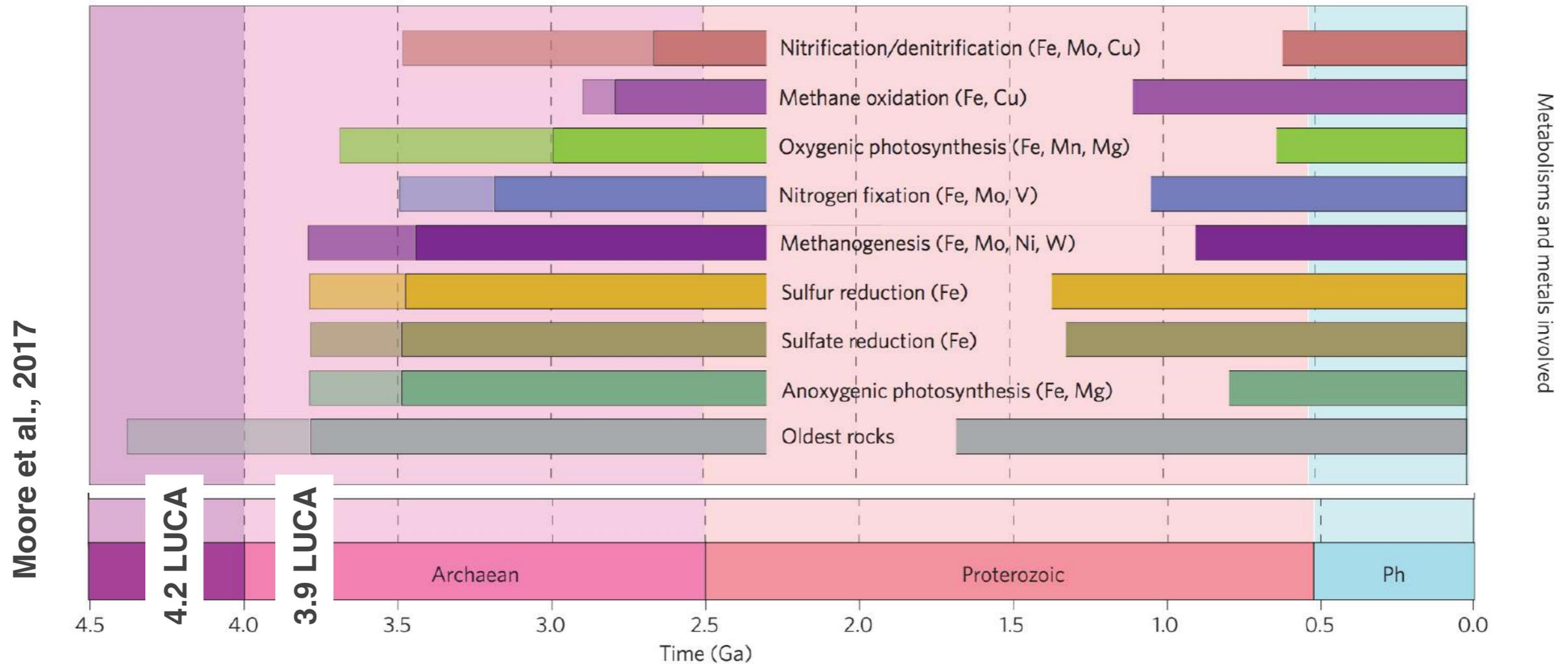


Table 3.2 Nutritional categories of microorganisms

Energy source	Carbon source	Hydrogen or electron source	Representative examples
Photolithoautotrophy			
Light	CO ₂	Inorganic	Cyanobacteria Purple sulfur bacteria Phototrophic protists
Photoorganoheterotrophy			
Light	Organic compounds	Organic compounds or H ₂	Purple non-sulfur bacteria Aerobic anoxygenic bacteria Proteorhodopsin-containing bacteria and archaea ^a
Chemolithoautotrophy			
Inorganic	CO ₂	Inorganic	Sulfur-oxidizing bacteria Hydrogen bacteria Methanogens Nitrifying bacteria and archaea
Chemoorganoheterotrophy			
Organic compounds	Organic compounds	Organic compounds	Wide range of bacteria and archaea Fungi Phagotrophic protists
Mixotrophy (combination of lithoautotrophy and organoheterotrophy)			
Inorganic	Organic compounds	Inorganic	Some sulfur-oxidizing bacteria, e.g. <i>Beggiatoa</i>
Mixotrophy (combination of photoautotrophy and organoheterotrophy)			
Light + organic compounds	CO ₂ + organic compounds	Inorganic or organic	Phagotrophic photosynthetic protists (some flagellates and dinoflagellates)

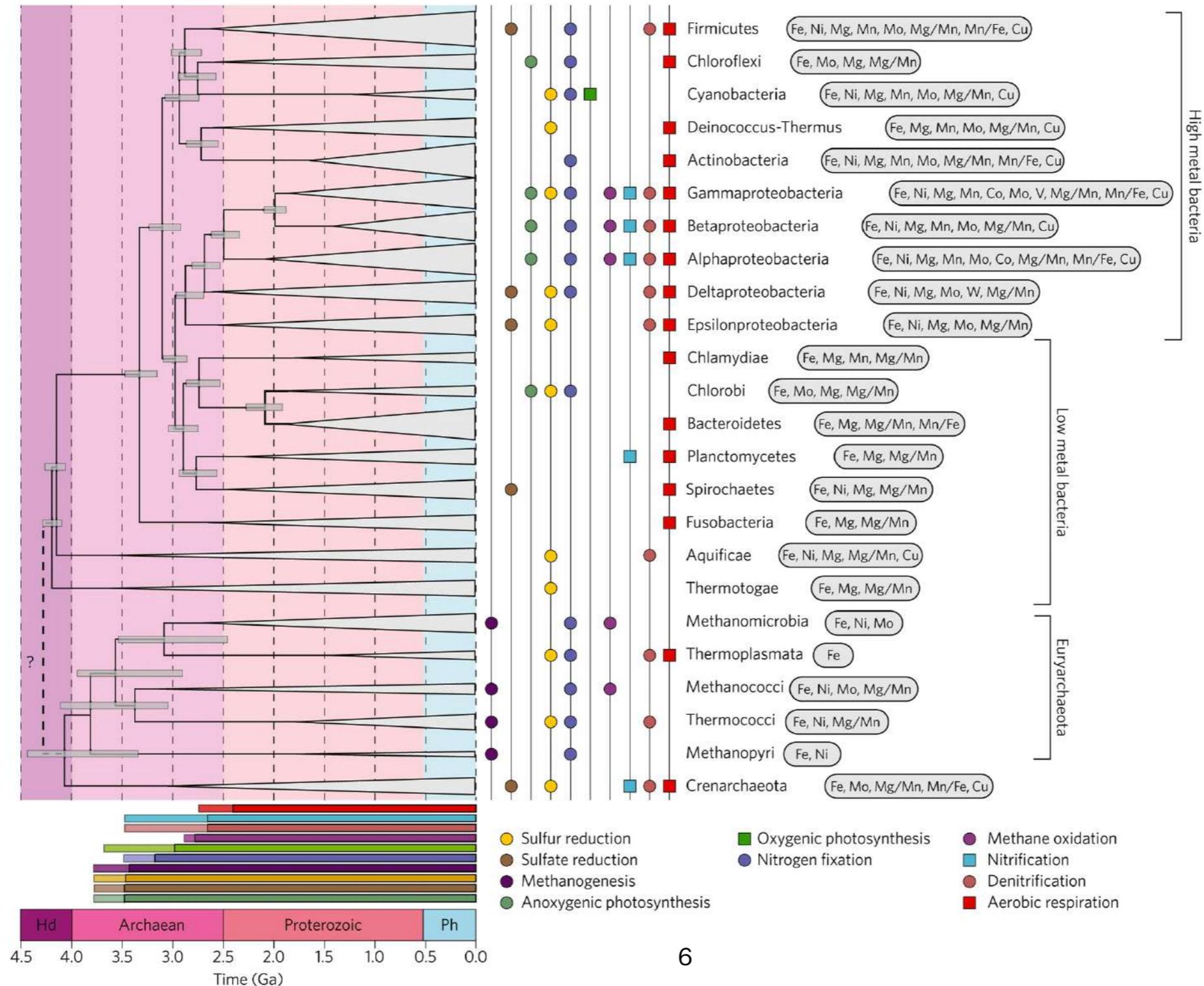
Microbial metabolisms in biogeochemical C cycle



- The availability of different metals and substrates has changed over the course of Earth's history as a result of secular changes in redox conditions of the mantle
- Solar energy used by early microbes
- The oxidoreductases responsible for these metabolisms incorporated metals that were readily available in Archaean oceans: iron and iron–sulfur clusters

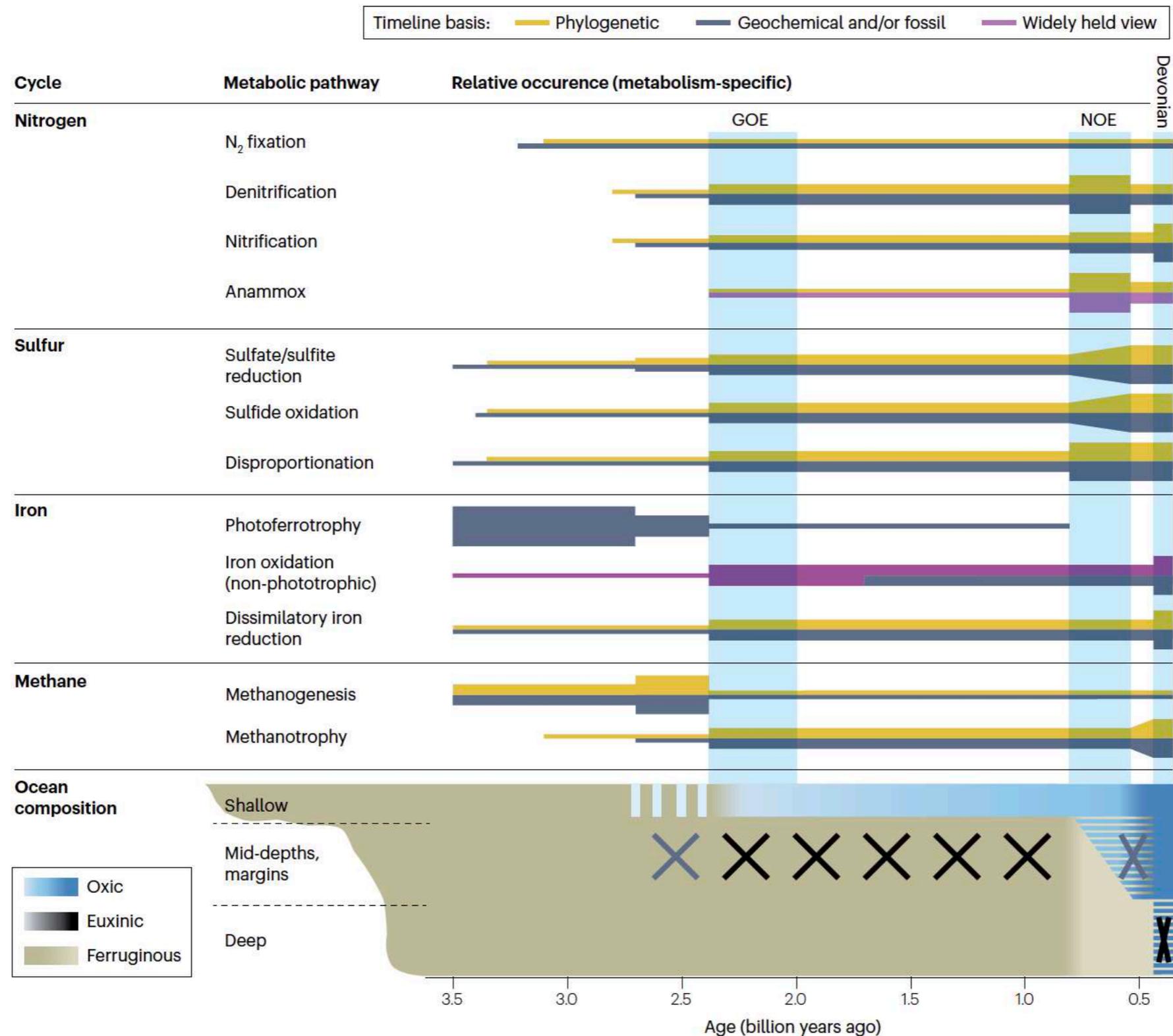
Phylogenetic tree of the main lineages of Bacteria and Archaea and their putative divergence times

Moore et al., 2017



Co-evolution of oceans and microbial pathways on Earth through time

Lyons et al., 2024



Key concepts for Microbial Life

- **Metabolic diversity:** cellular processes that support growth
Energy is conserved from chemical reaction or from light
 - ★ **Energy is conserved, reducing power is obtain during catabolic reactions and cells growth by decoupling this power to anabolic-biosynthetic reactions (modularity)**
 - ★ **Electron flow via redox provide energy for ATP synthesis via:**
 1. **Substrate level phosphorylation**
 2. **Oxidative phosphorylation**
 3. **Photophosphorilation**
- **Ecological diversity:** interactions between organisms and their environments
- **Phylogenetic diversity:** evolutionary relationships between organisms

LIVING vs NON living

You are alive if you have:

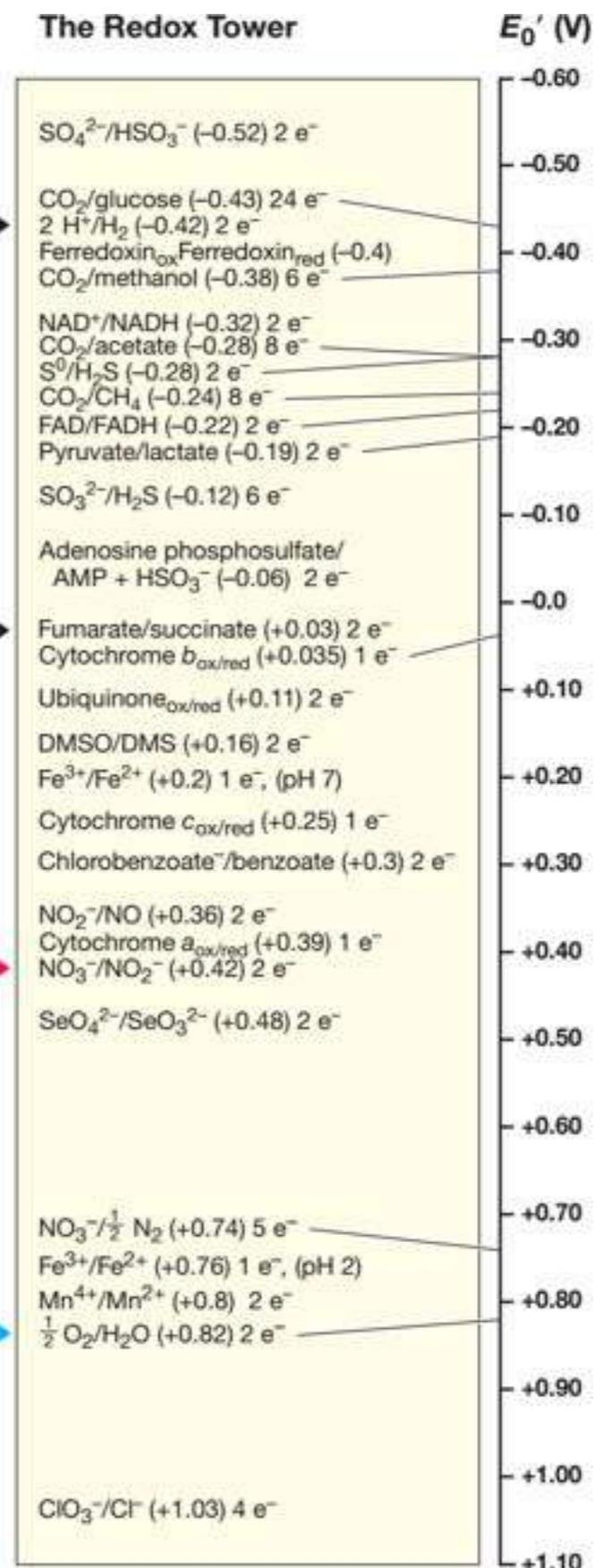
1. A membrane subsystem for compartmentalizing the functional network components
2. An autocatalytic metabolic subsystem that functions out-of-equilibrium by capturing energy and material resources
3. An information-based subsystem for processing and transferring genetic information to the progeny via self-replication

Ganti, T. in The Principles of Life (ed. Szathmary, E. and Griesemer, J.) Ch. 3(Oxford Univ. Press, Oxford 2003)

Redox reaction for microbial growth

- To predict if coupled reactions are sufficiently energetic to produce growth the voltage of the half reaction of electron donor should differ of about **-200 mV** from the voltage of electron acceptor \rightarrow for **ATP production**
- The **strongest donors** at the top ($E_0' < 0$)
- The **strongest acceptors** at the bottom ($E_0' > 0$)

Reduced



Oxidized

Energy yield for microbial growth, I

- To predict if the reactions are sufficiently energetic to produce growth the energy yield must be high: -31.8kJ equal to $\sim 8 \text{ kcal}$ for **ATP production**

Energy-Yielding Reactions Involving C, N and S	$\Delta G^{0'} = \text{kJ/Reaction}$
Carbon Cycle	
Glucose + 6O ₂ → 6H ₂ O + 6CO ₂	-2,870.0
Glucose → 2 ethanol + 2CO ₂	-238.8
Glucose → 2 lactate + H ⁺	-196.0
4H ₂ + CO ₂ → CH ₄ + 2H ₂ O	-136.0
4H ₂ + 2 CO ₂ → acetic acid + 2H ₂ O	-104.8
H ₂ + fumarate → succinate	-86.2
Acetic acid → CH ₄ + CO ₂	-37.0
Nitrogen Cycle	
Glucose + 8NO ₂ ⁻ + 8H ⁺ → 6CO ₂ + 4N ₂ + 10H ₂ O	-3,144.0
3H ₂ + NO ₂ ⁻ + 2H ⁺ → NH ₄ ⁺ + 2H ₂ O	-436.8
NH ₃ + 2O ₂ → NO ₂ ⁻ + 2H ⁺ + 2H ₂ O	-266.7
Sulfur Cycle	
S ²⁻ + 2O ₂ → SO ₄ ²⁻	-790.5
S ⁰ + 1.5O ₂ + H ₂ O → SO ₄ ²⁻ + 2H ⁺	-580.9
4H ₂ + SO ₄ ²⁻ → HS ⁻ + 3H ₂ O + OH ⁻	-152.0
Acetate + SO ₄ ²⁻ + 3H ⁺ → 2CO ₂ + HS ⁻ + 2H ₂ O + H ⁺	-57.5
2H ₂ + S ⁰ → HS ⁻ + H ⁺	-29.0

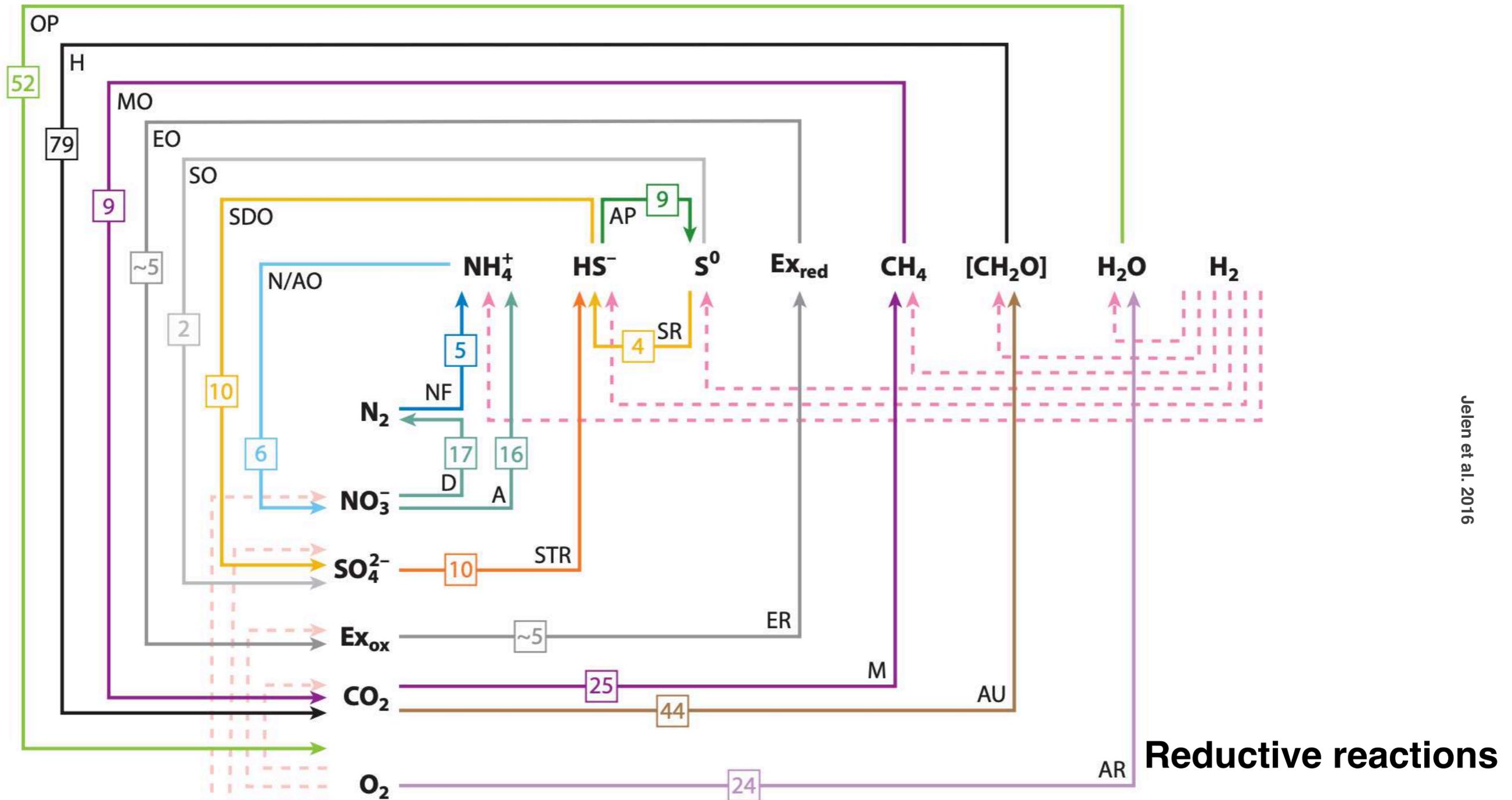
Energy yield for microbial growth, II

- To predict if the reactions are sufficiently energetic to produce growth the energy yield must be high: -31.8kJ equal to $\sim 8 \text{ kcal}$ for **ATP production**

Energy-Yielding Reactions Involving Fe, Mn, Se, and As		$AG^{\circ\prime} = \text{kJ/Reaction}$
Iron reactions		
$\text{Acetate} + 8\text{Fe}^{3+} + 4\text{H}_2\text{O} \rightarrow 2\text{HCO}_3^- + 8\text{Fe}^{2+} + 9\text{H}^+$		-233.0
$\text{Fe}^{2+} + 0.25\text{O}_2 + \text{H}^+ \rightarrow \text{Fe}^{3+} + 0.25\text{H}_2\text{O}$		-44.2
Manganese reactions		
$\text{MnO}_2 + 4\text{H}^+ + 2\text{e}^- \rightarrow \text{Mn}^{2+} + 2\text{H}_2\text{O}$		-233.0
$\text{Mn}^{2+} + 0.5\text{O}_2 + \text{H}_2\text{O} \rightarrow \text{MnO}_2 + 2\text{H}^+$		-44.2
Selenium reactions		
$\text{Lactate} + 2\text{SeO}_4^{2-} \rightarrow \text{acetate} + 2\text{SeO}_3^{2-} + \text{HCO}_3^- + \text{H}^+$		-343.1
$\text{Lactate} + 2\text{SeO}_3^{2-} + \text{H}^+ \rightarrow \text{acetate} + 2\text{Se}^0 + \text{HCO}_3^- + \text{H}_2\text{O}$		-529.5
Arsenic reactions		
$\text{Lactate} + 2\text{AsO}_4^{2-} + \text{H}^+ \rightarrow \text{acetate} + 2\text{H}_2\text{AsO}_3^- + \text{HCO}_3^-$		-140.3
$\text{Lactate} + 2\text{H}_2\text{AsO}_3^- \rightarrow \text{acetate} + 2\text{AsH}_3 + \text{HCO}_3^- + \text{H}^+$		-138.4

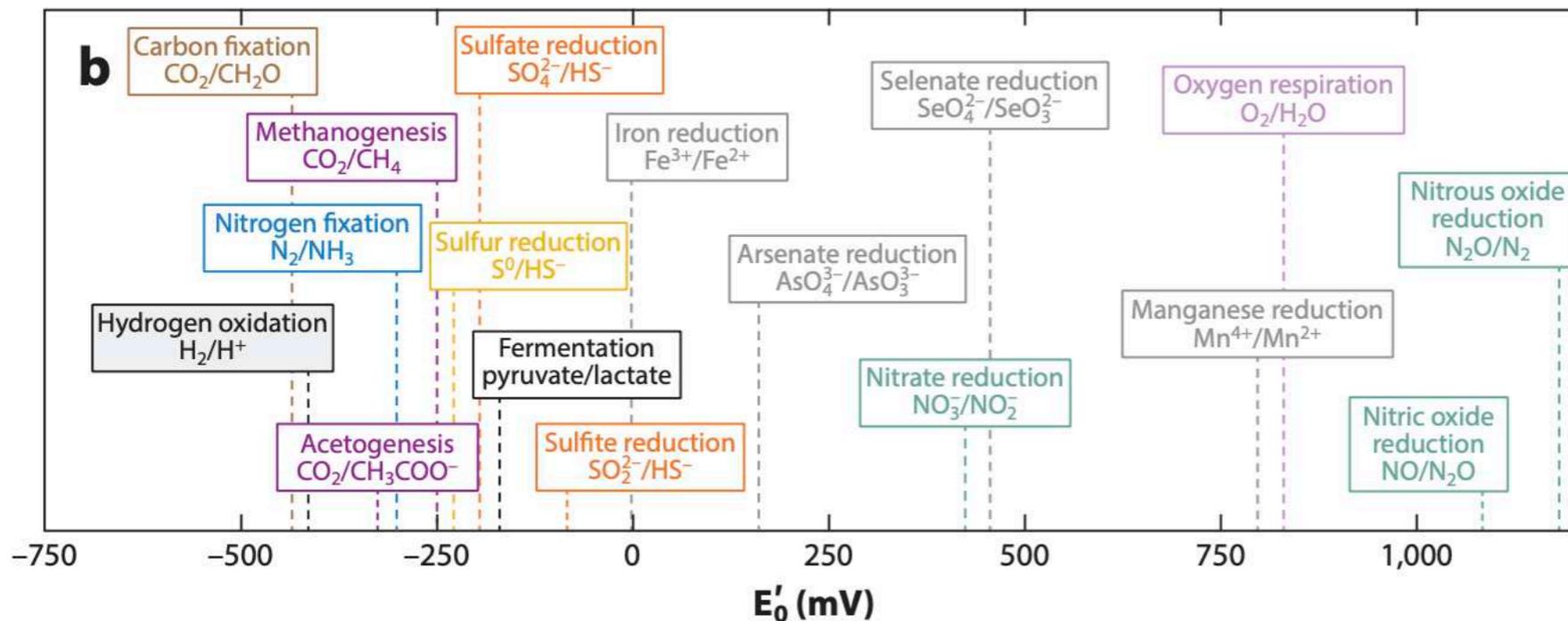
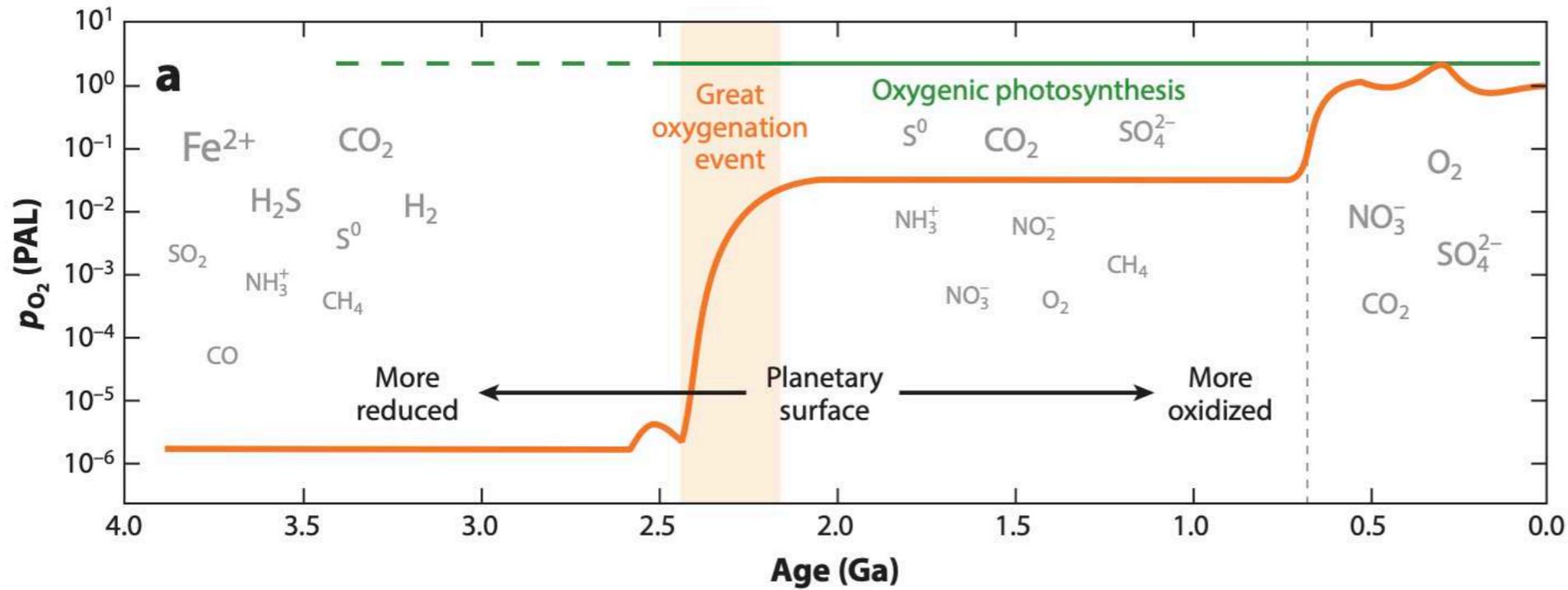
Integrative approach for studying microbial metabolisms

Oxidative reactions



A, ammonification; AP, anoxygenic photosynthesis; AR, aerobic respiration; AU, autotrophy; D, denitrification; Ex_{ox}, other elements oxidation; Ex_{red}, other elements reduction; H, heterotrophy; M, methanogenesis; MO, methane oxidation/methanotrophy; N/AO, nitrification/ammonia oxidation; NF, nitrogen fixation; OP, oxygenic photosynthesis; SDO, sulfide oxidation; SO, sulfur oxidation; SR, sulfur reduction; STR, sulfate reduction

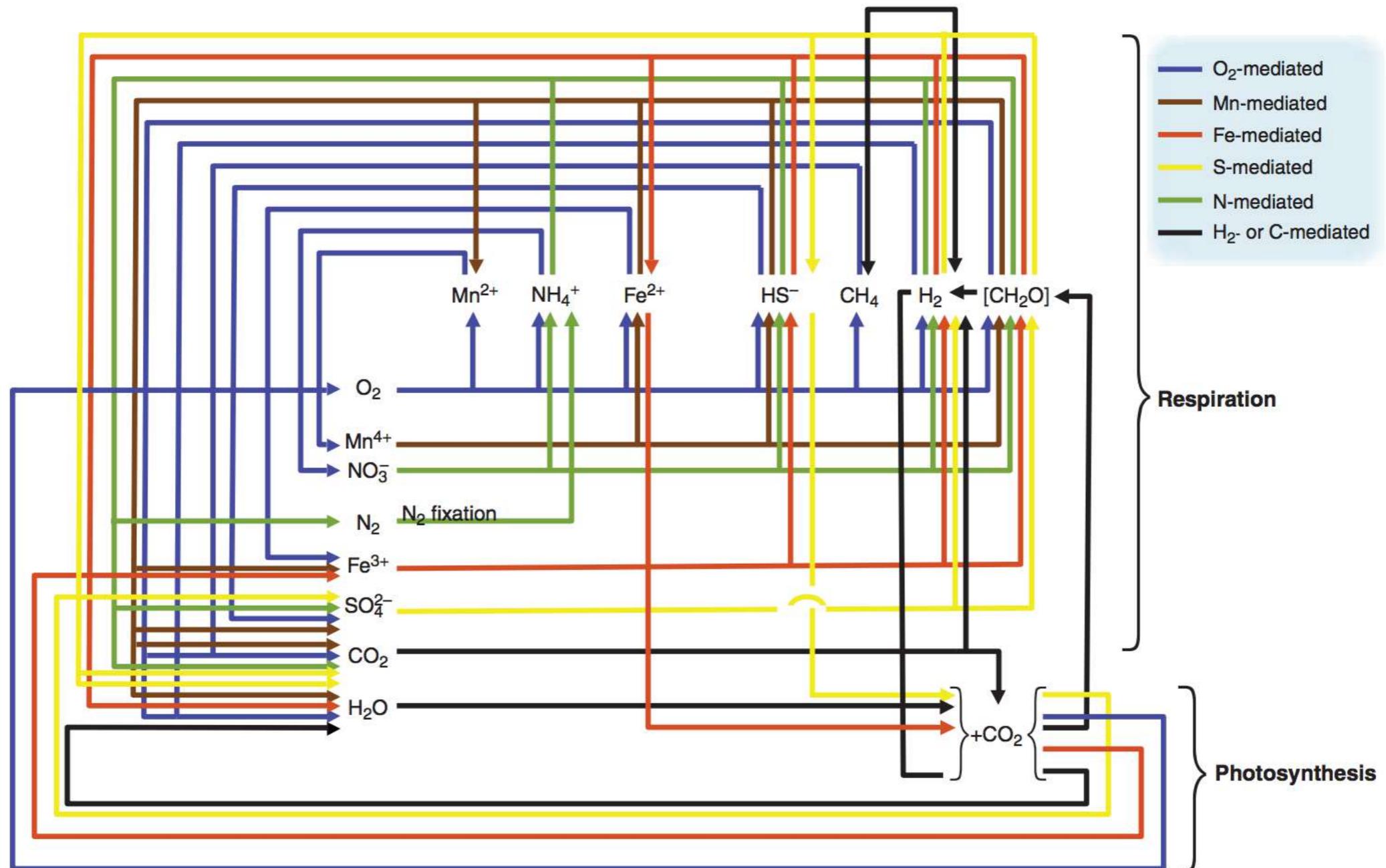
Coevolution of geosphere and biosphere through time as depicted by change in planetary redox state, availability of redox couples



Standard reduction potential at pH 7 (E'_0) of biologically relevant redox pairs. Redox halfreactions represent the reductive side (i.e., terminal electron acceptor) of given pathways

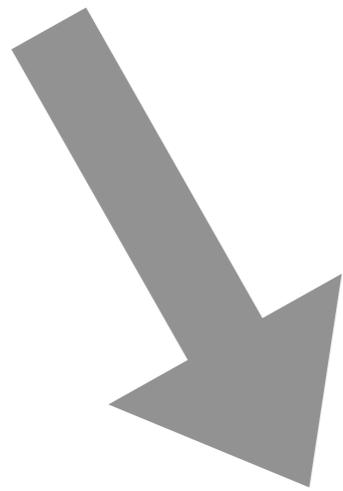
Global microbial metabolism on Earth

Falkowski et al., 2008

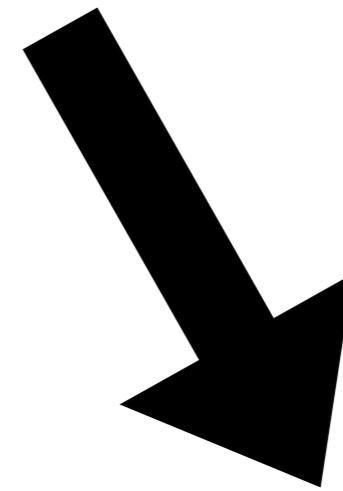


- A global, interconnected network of the biologically mediated cycles for hydrogen, carbon, nitrogen, oxygen, sulfur, and iron
- A large portion of these microbially mediated processes are associated only with anaerobic habitats

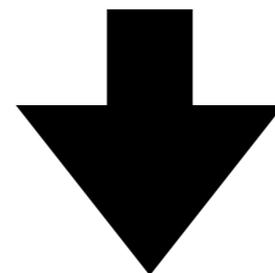
**Microbes obtain energy from
light or oxidation of compounds**



Phototrophy



Chemotrophy

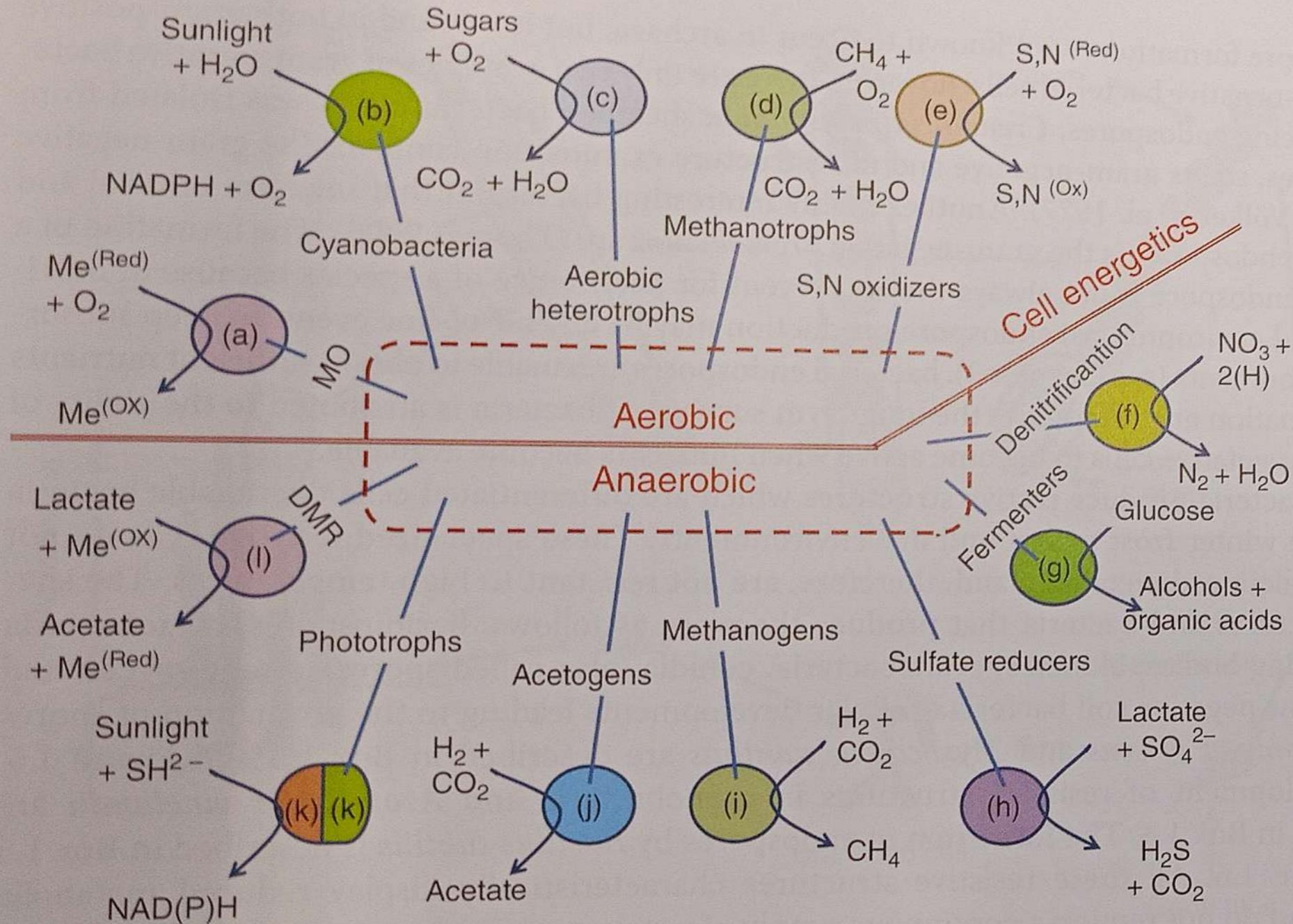


ATP synthesis

Phototrophy & Chemotrophy

Aerobic metal oxidizers

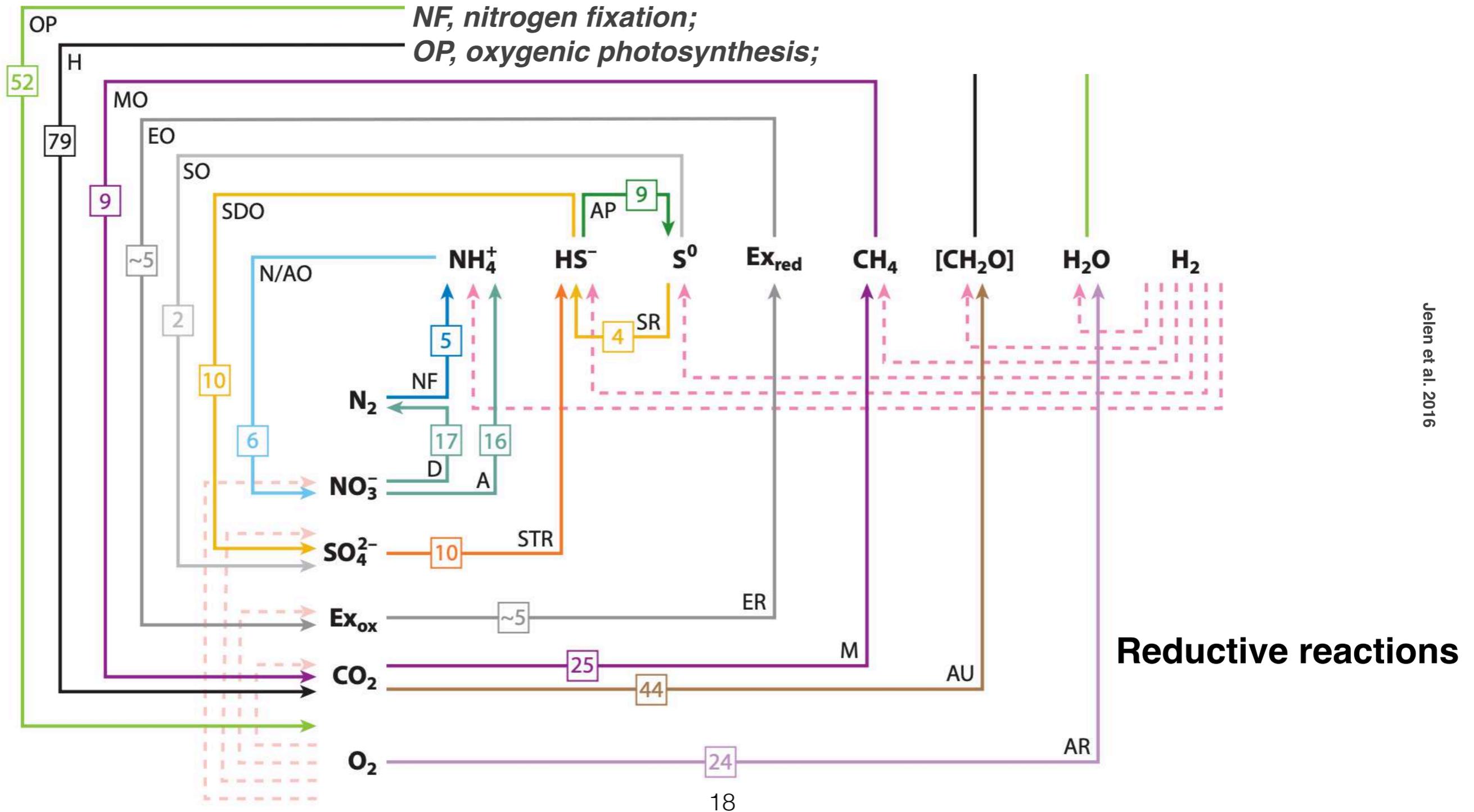
Dissimilatory metal reduction



Photosynthesis and N₂ fixation

Oxidative reactions

AP, anoxygenic photosynthesis;
AU, autotrophy;
Exox, other elements oxidation; Exred, other elements reduction;
H, heterotrophy;
NF, nitrogen fixation;
OP, oxygenic photosynthesis;



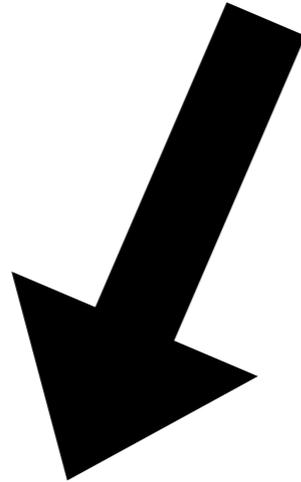
Phototrophy

- Oxygenic Photosynthesis
- Anaerobic Anoxygenic Photosynthesis
- Aerobic Anoxygenic Photosynthesis

Phototrophy

- Oxygenic Photosynthesis: light, CO_2 , **H_2O as electron donor** and O_2 production, biomass with Mg-containing pigments: Chlorophylls in **Cyanobacteria and Eukarya** —> **lit surfaces and water column, autotrophs**
- Anaerobic Anoxygenic Photosynthesis: light, CO_2 , **H_2S , S^0 , $\text{H}_2\text{SO}_3^{2-}$, H_2 as electron donors**, biomass with Mg-containing pigment as bacteriochlorophyll in **purple sulfur bacteria** —> **shallow sediment and microbial mats, autotrophs**
- Aerobic Anoxygenic Photosynthesis: light, CO_2 , live in presence of O_2 , **are heterotrophs, (no enzyme to fix C in biomass)** in **AAnP** up to 20% in upper water column in oligotrophic areas

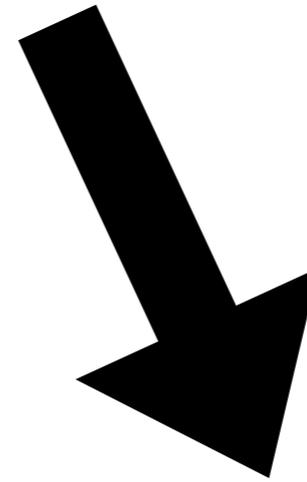
Carbon fixation



Calvin-Benson-Bassham

RuBisCO, cycle to produce the substrate that take up CO₂ molecule, 6 CO₂ for a 6-C-sugar

ATP and NADH requirements



Reverse tricarboxylic acid cycle

Acetyl-coA-pathway

Wood-Ljungdahl pathway

Hydroxypropionate Cycle

Deep see sediment, vents and symbionts

Annamox bacteria

Methanogens, acetate-producing microbes in anaerobic sediments

Hyper saline environment

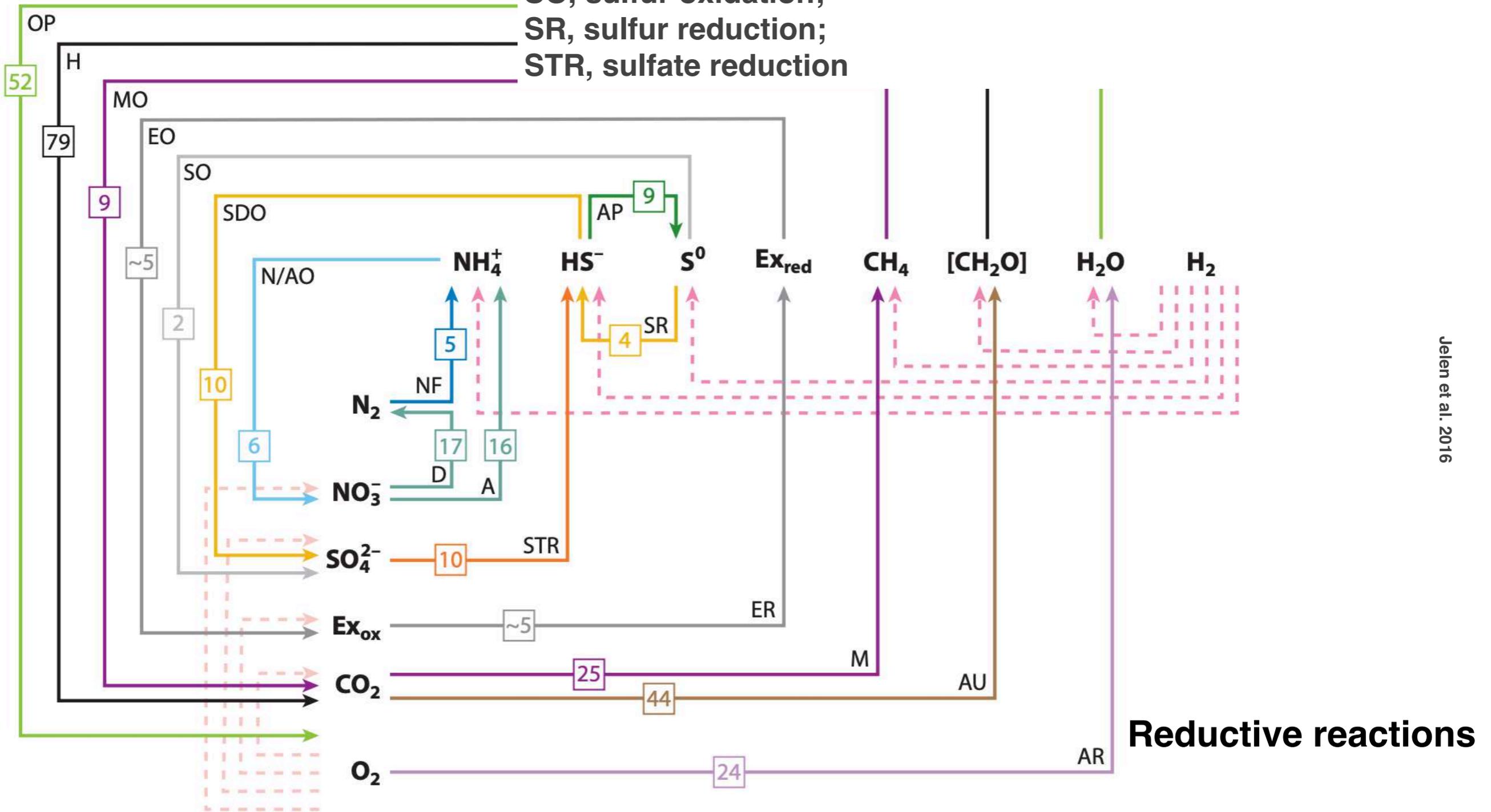
Nitrogen fixation

- Abiotic fixation by lightning 5-8%
- **Diazotrophy (nitrogen fixation): reduction of N_2 to NH_3**
- **Difficult reaction** due to triple bond N_2
- 18 ATP requirements
- **O_2 sensitive, ancient metabolism \rightarrow Nitrogenase complex**
- **Diverse co-factors**

- Nitrogen-fixing microbes: Bacteria and Archaea
- Photo-Chemo- lithoauto- and chemoorganotrophs
- Cyanobacteria, archaea methanogens

Oxidative reactions

A, ammonification;
D, denitrification;
M, methanogenesis;
MO, methane oxidation/methanotrophy;
N/AO, nitrification/ammonia oxidation;
SDO, sulfide oxidation;
SO, sulfur oxidation;
SR, sulfur reduction;
STR, sulfate reduction



Chemotrophy

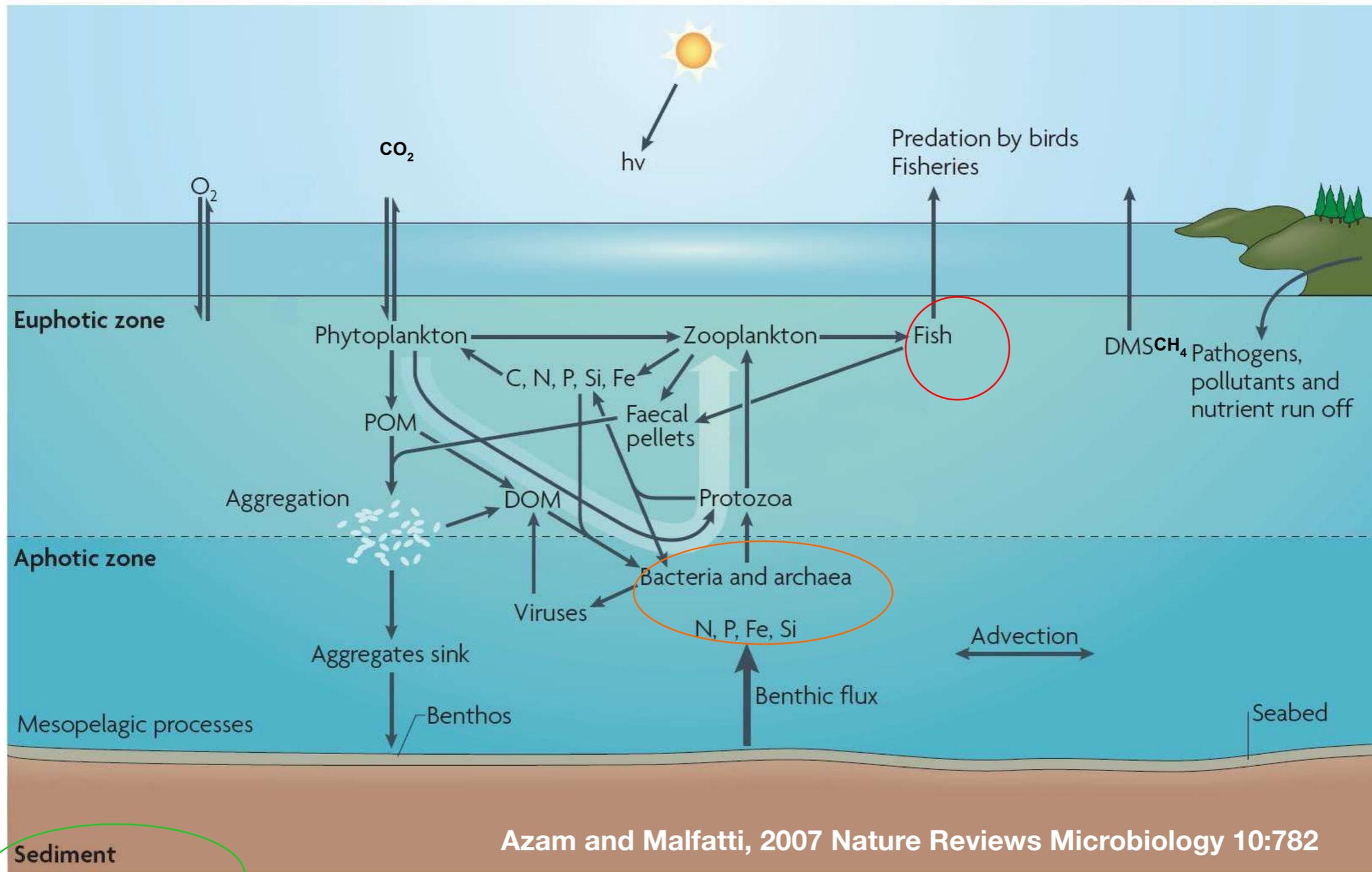
- Chemolithotrophs: ATP synthesis via electron transport chain with **S⁰, sulfide, H₂, NH₄⁺, NO₂⁻ (nitrite) and Fe²⁺ as electron donors** in sediment, hydrothermal vents and water column
 - Low ATP yield, need to oxidize large quantities
 - Coupled with O₂ or **NO₃⁻** as electron acceptor
 - Bacteria and Archaea

Chemotrophy II

- * *H₂-oxidizing bacteria*
- * *Sulfur Oxidizing Bacteria (SOB)*
- * *Sulfate Reducing Bacteria (SRB)*
- * *Nitrification*
- * *Fermentaion*
- * *Denitrification*
- * *Anaerobic Ammonia oxidation (annamox)*

**Where do we find these
microbial metabolisms?...
a metagenomic question**

Marine biogeochemical C cycle



Microbial energy generating metabolic pathways shaping Earth ecosystem

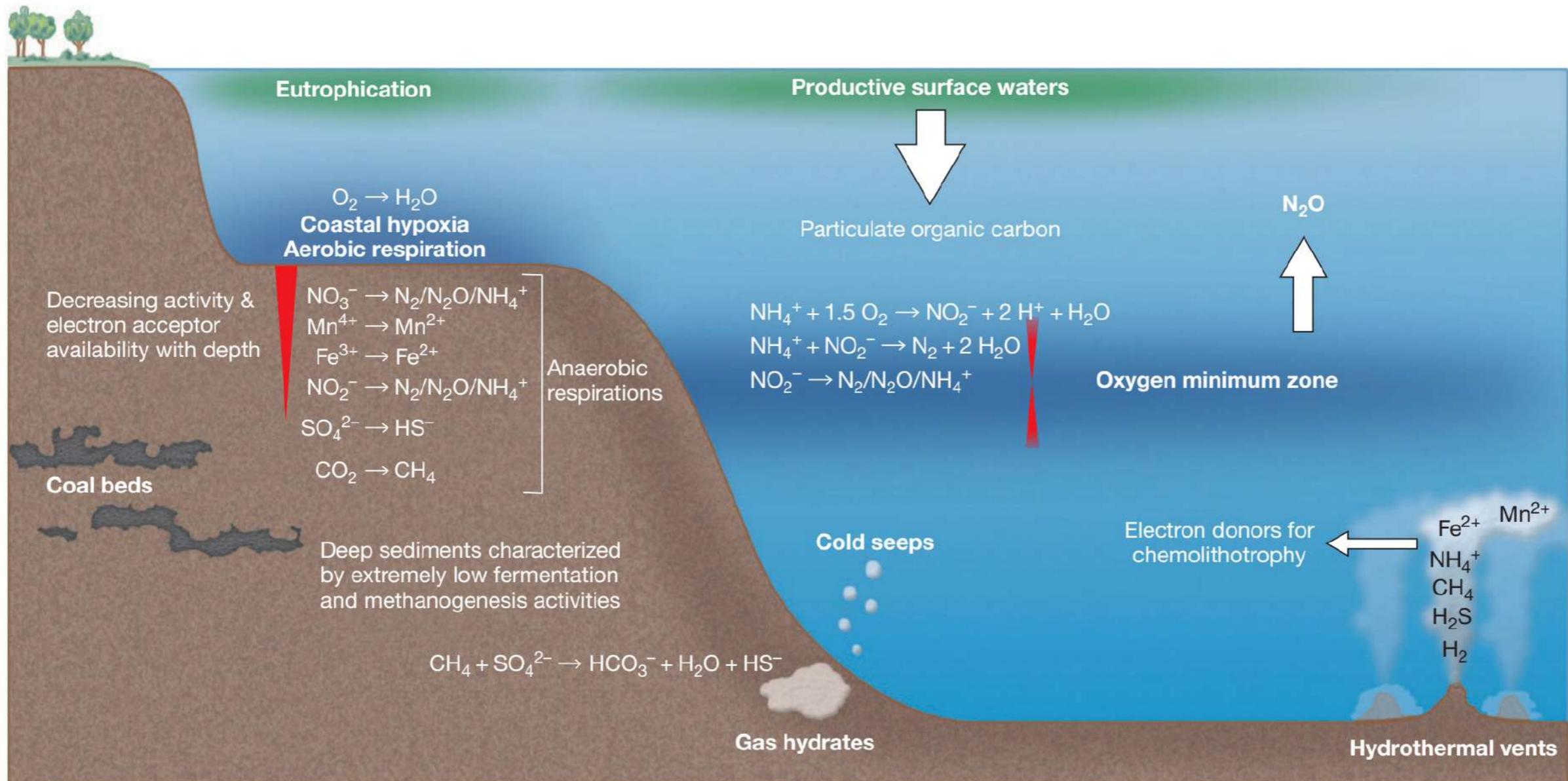
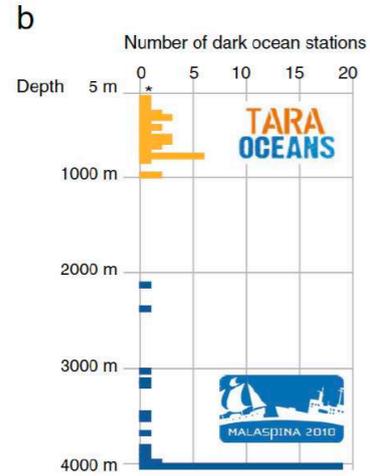


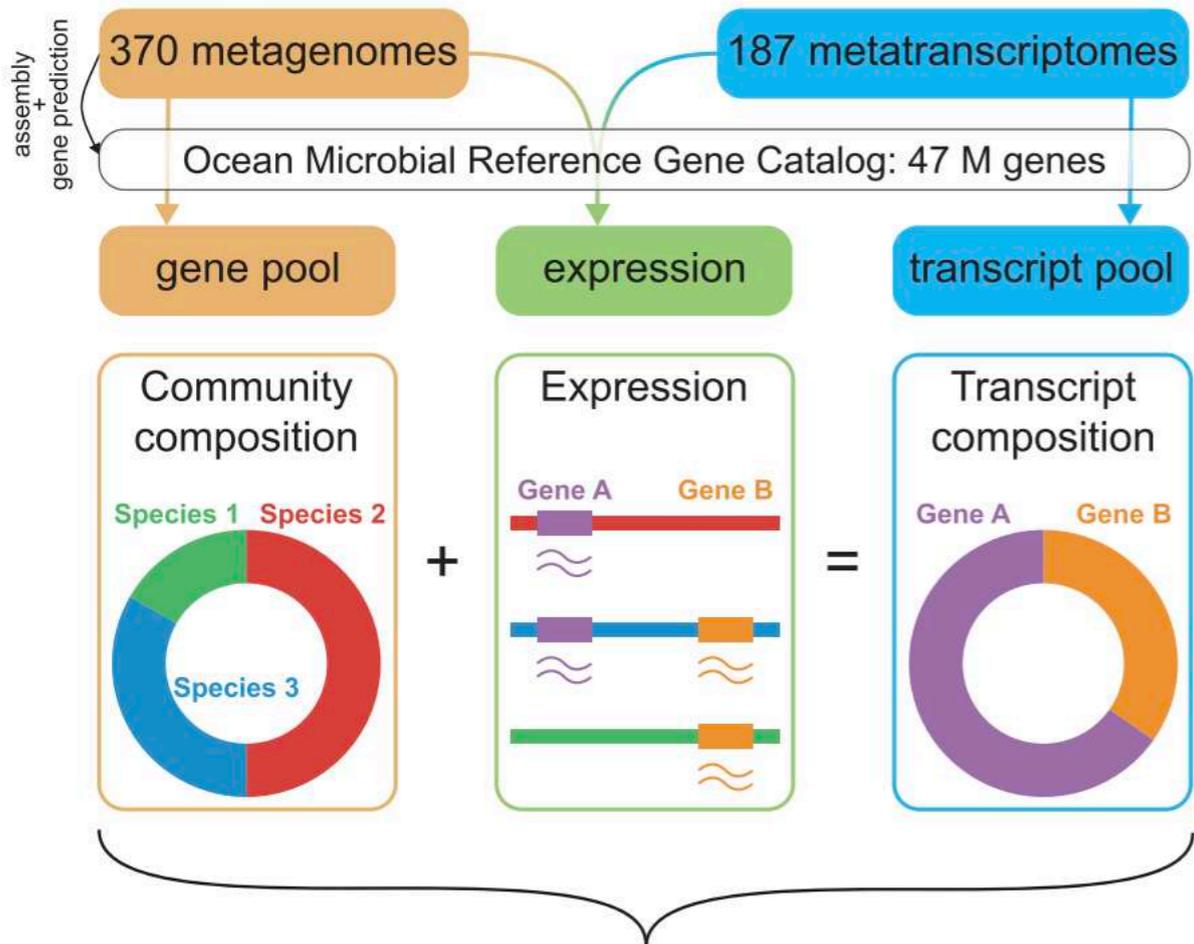
Figure 20.20 Diversity of marine systems and associated microbial metabolic processes. Decreasing electron acceptor availability with depth into the sediment or with increasing distance into an oxygen minimum zone is indicated by red wedges. Sulfate becomes limiting only at greater depths in marine sediments. The indicated metabolic diversity is covered in Chapter 14.

Madigan et al. 2018

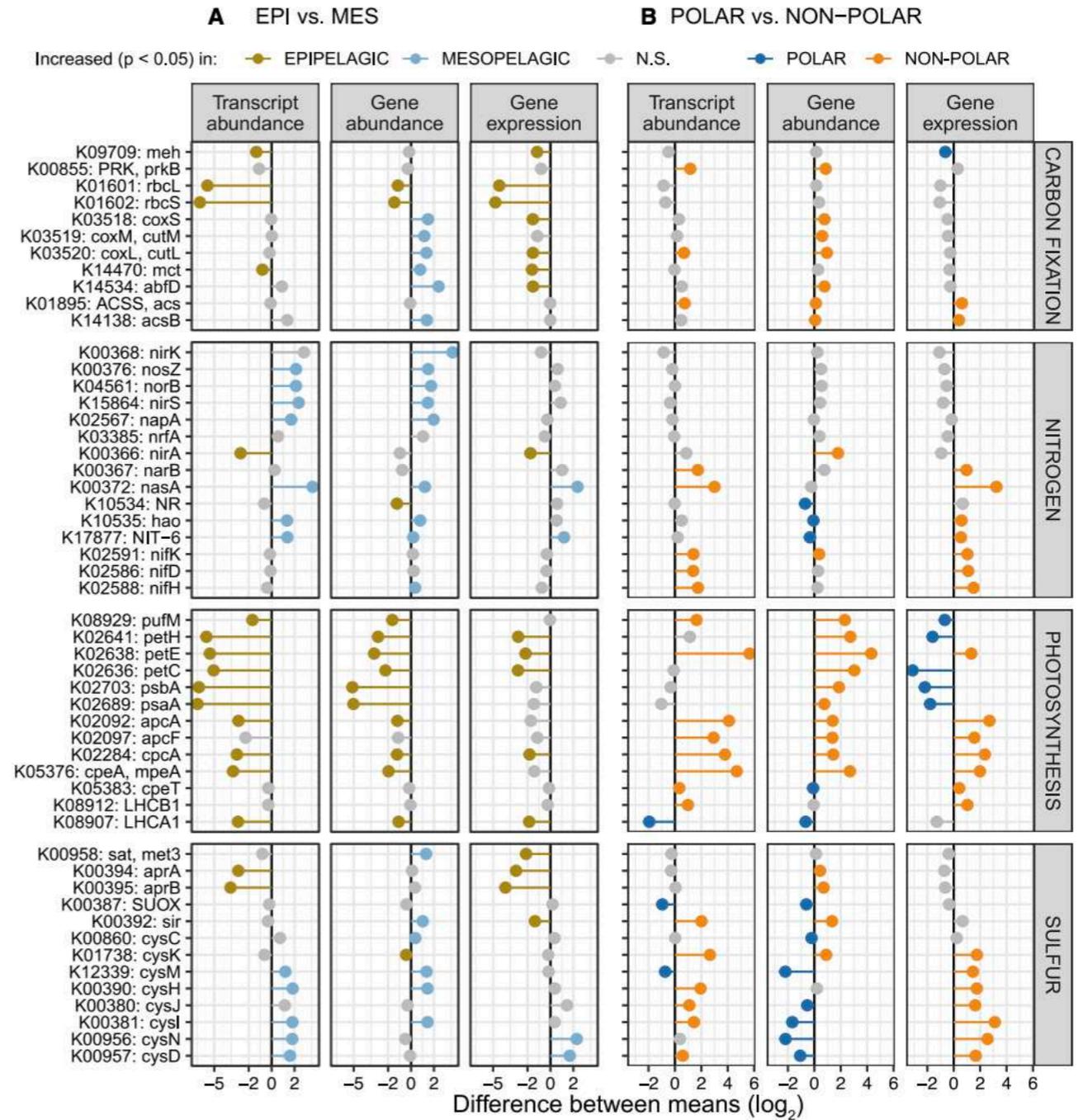
Metabolic pathways in microbial communities from surface ocean Tara



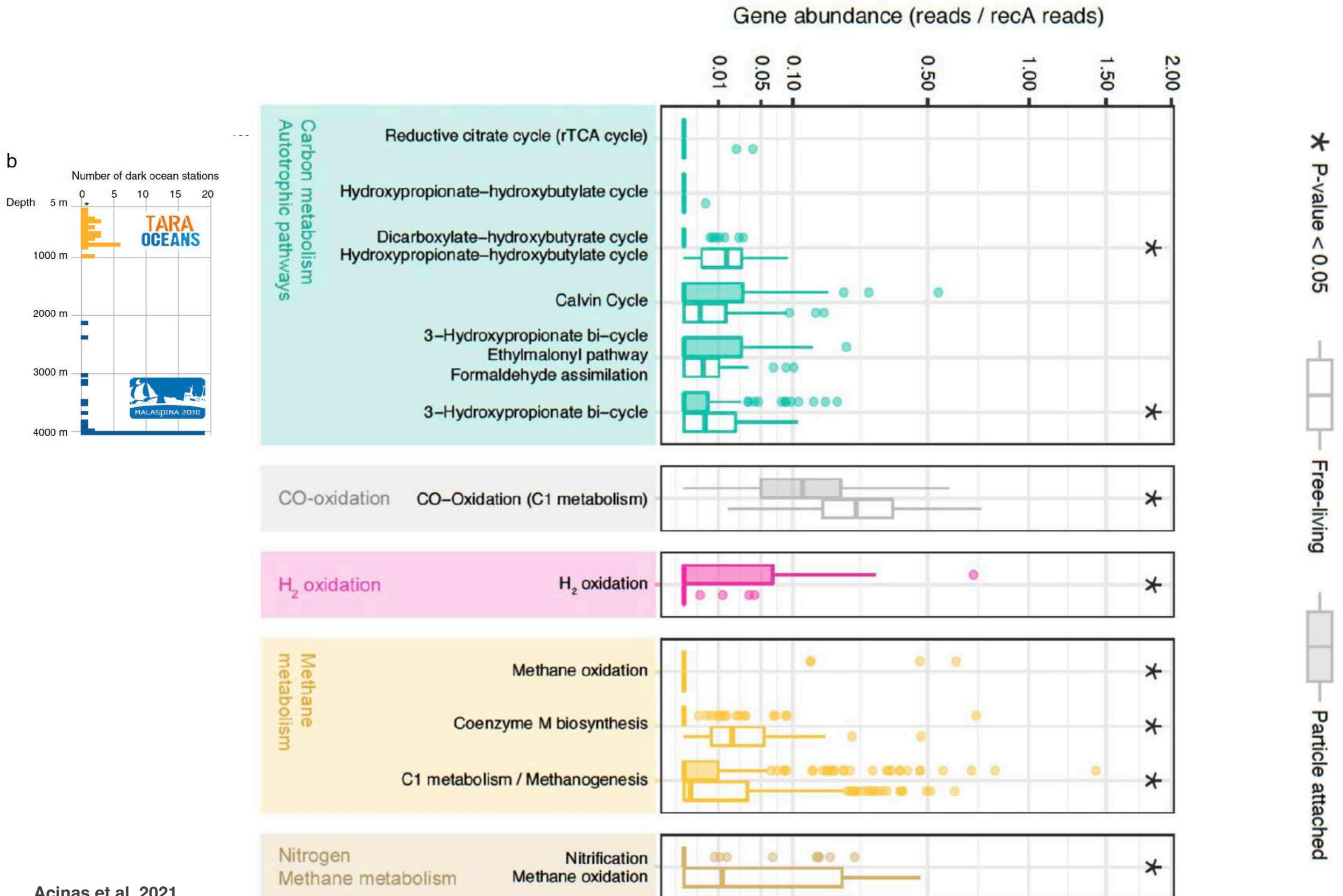
Acinas et al. 2021



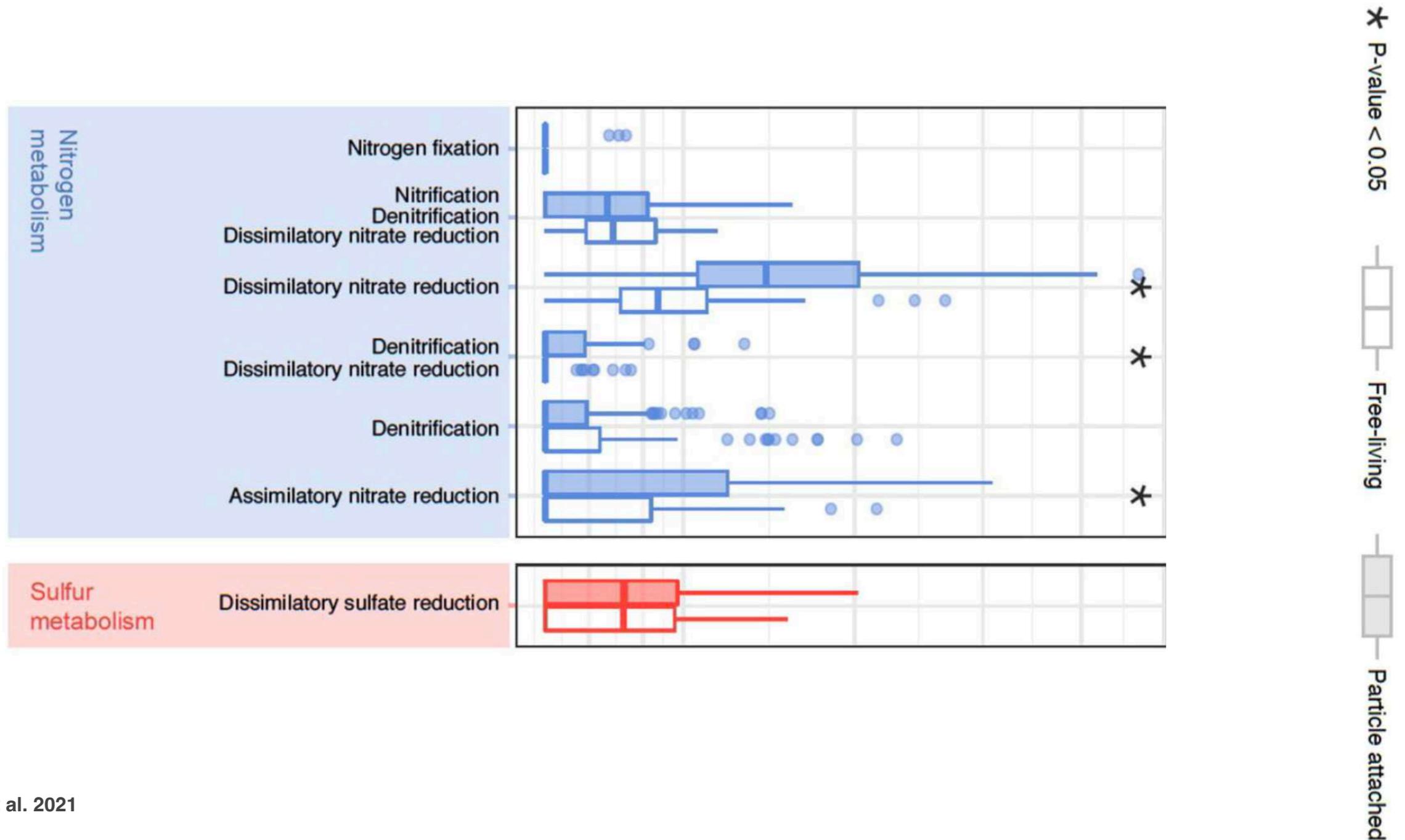
Salazar et al. 2019



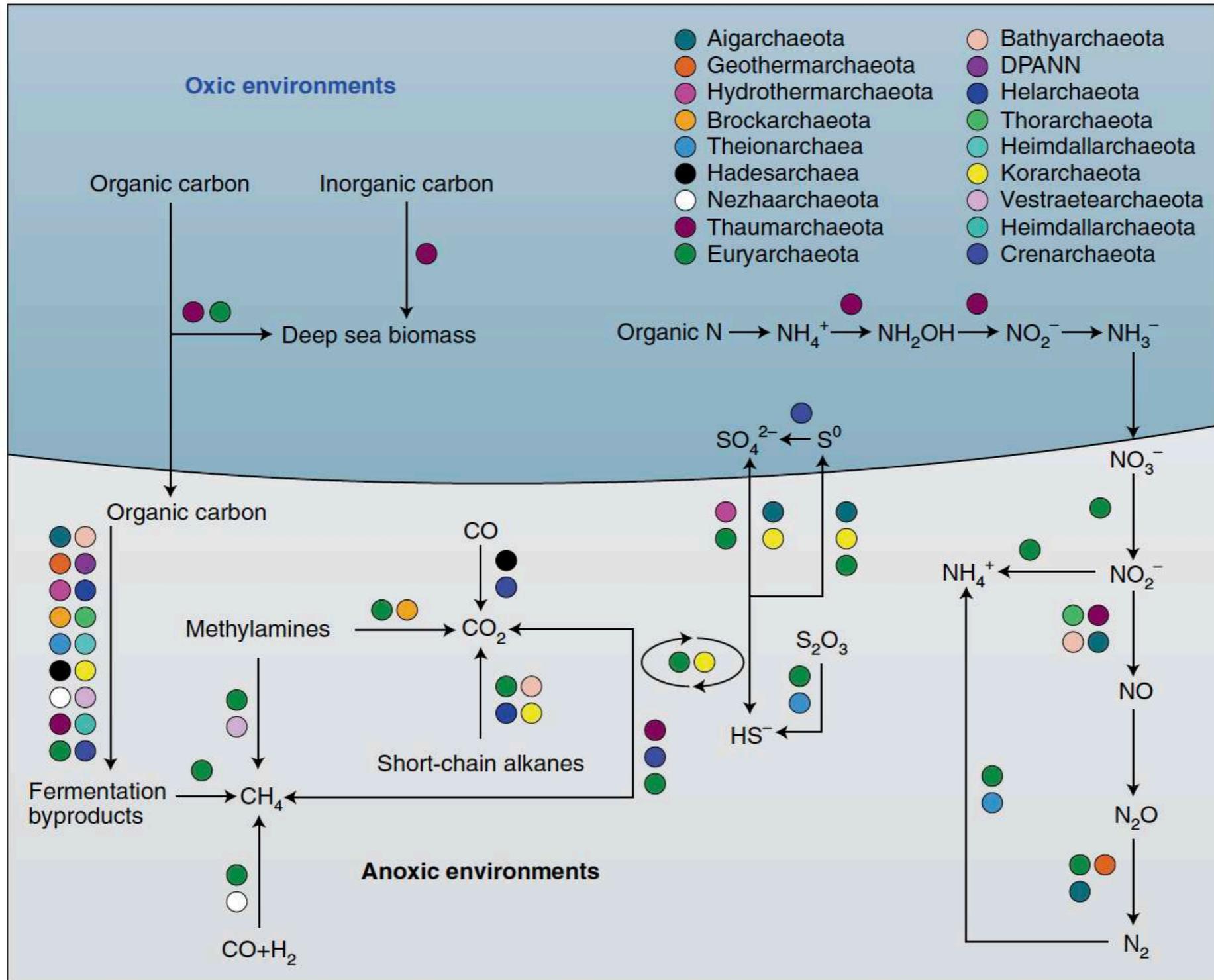
Metabolic pathways in the free-living and particle-attached microbial communities from dark ocean-Malaspina I



Metabolic pathways in the free-living and particle-attached microbial communities from dark ocean-Malaspina II



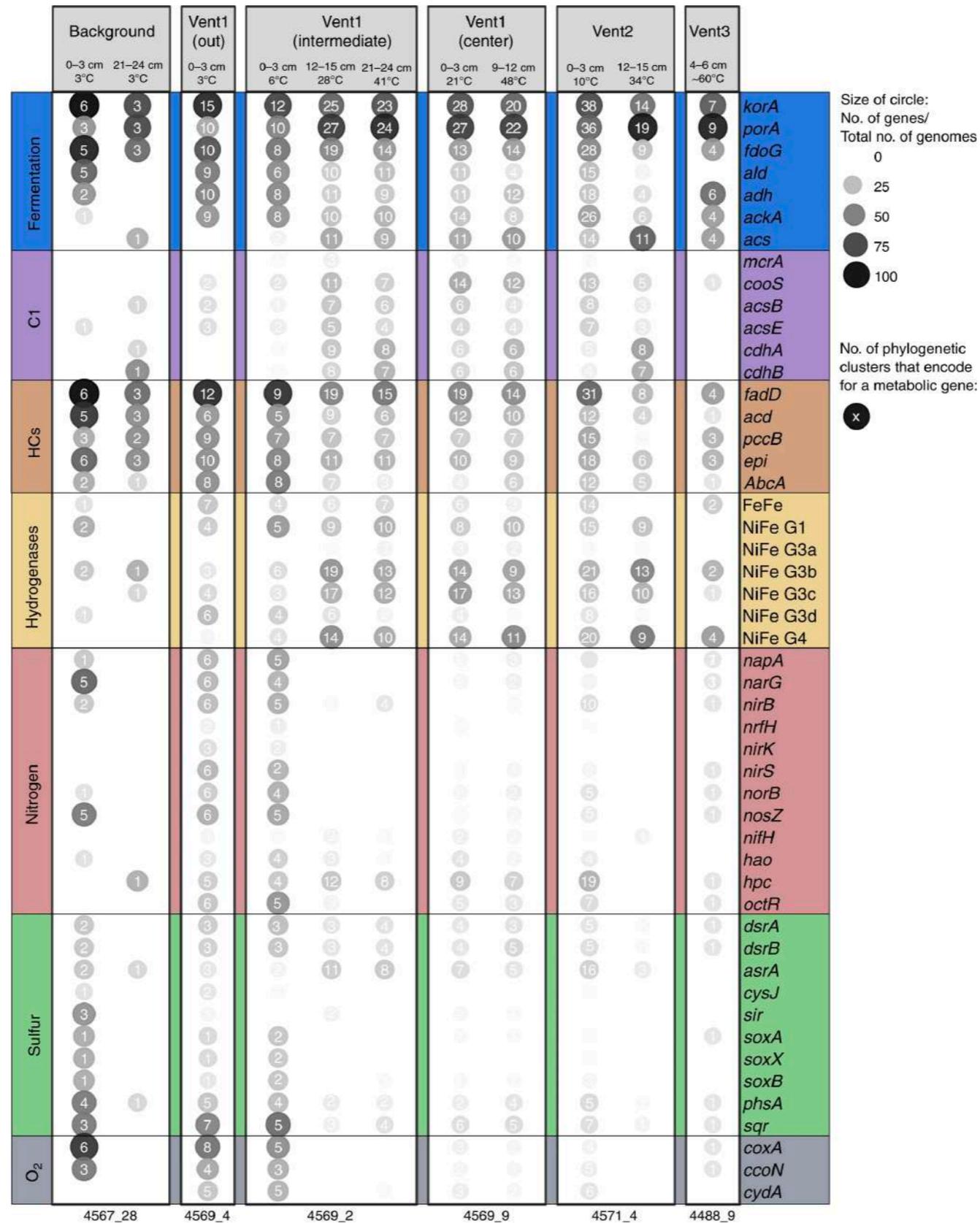
Archaeal ecological roles



Baker et al. 2020

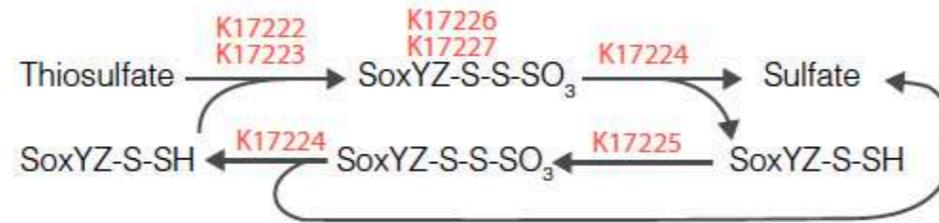
Metabolic profile of sediment microbial community

Dombrowski et al. 2018

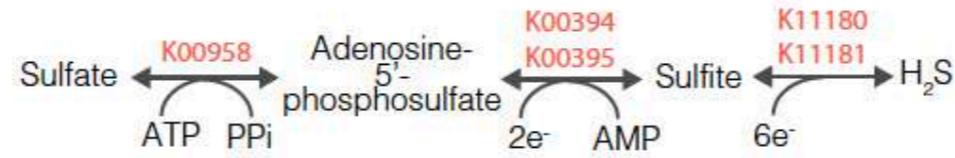


Sulfur metabolism

Thiosulfate oxidation by SOX complex

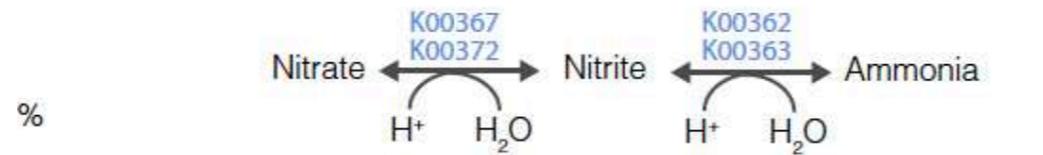


Dissimilatory sulfate reduction

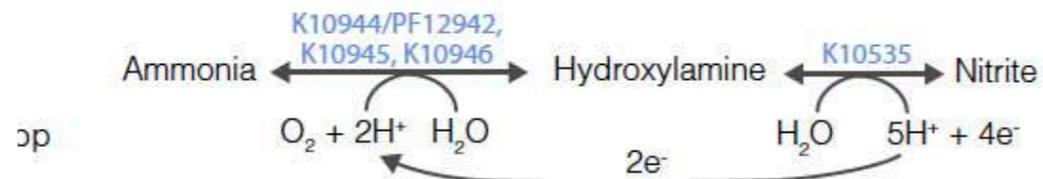


Nitrogen metabolism

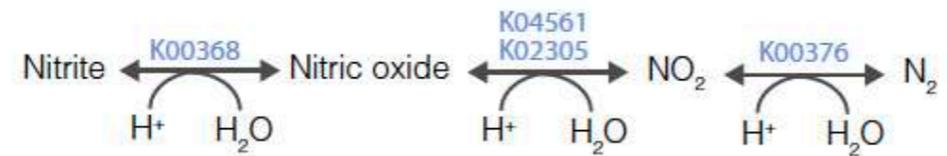
Assimilatory / Dissimilatory nitrate reduction



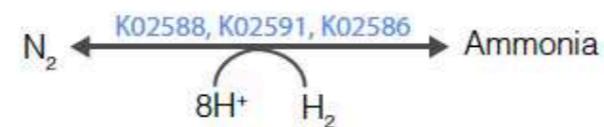
Nitrification



Denitrification

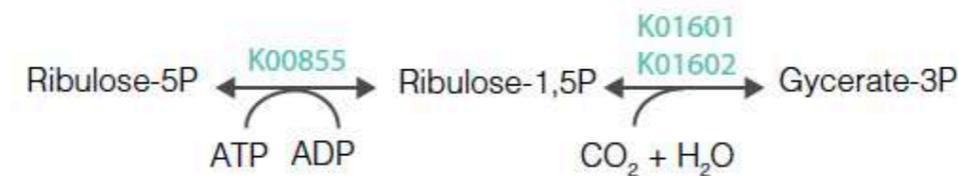


Nitrogen fixation

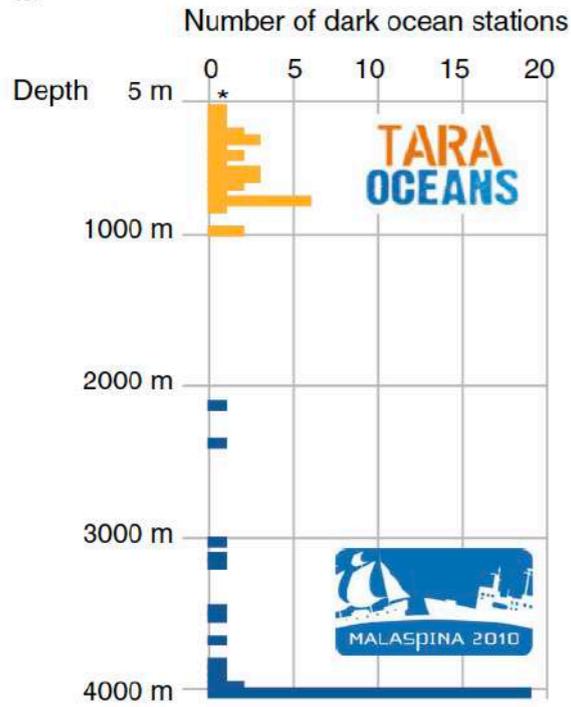


Carbon fixation

Calvin cycle

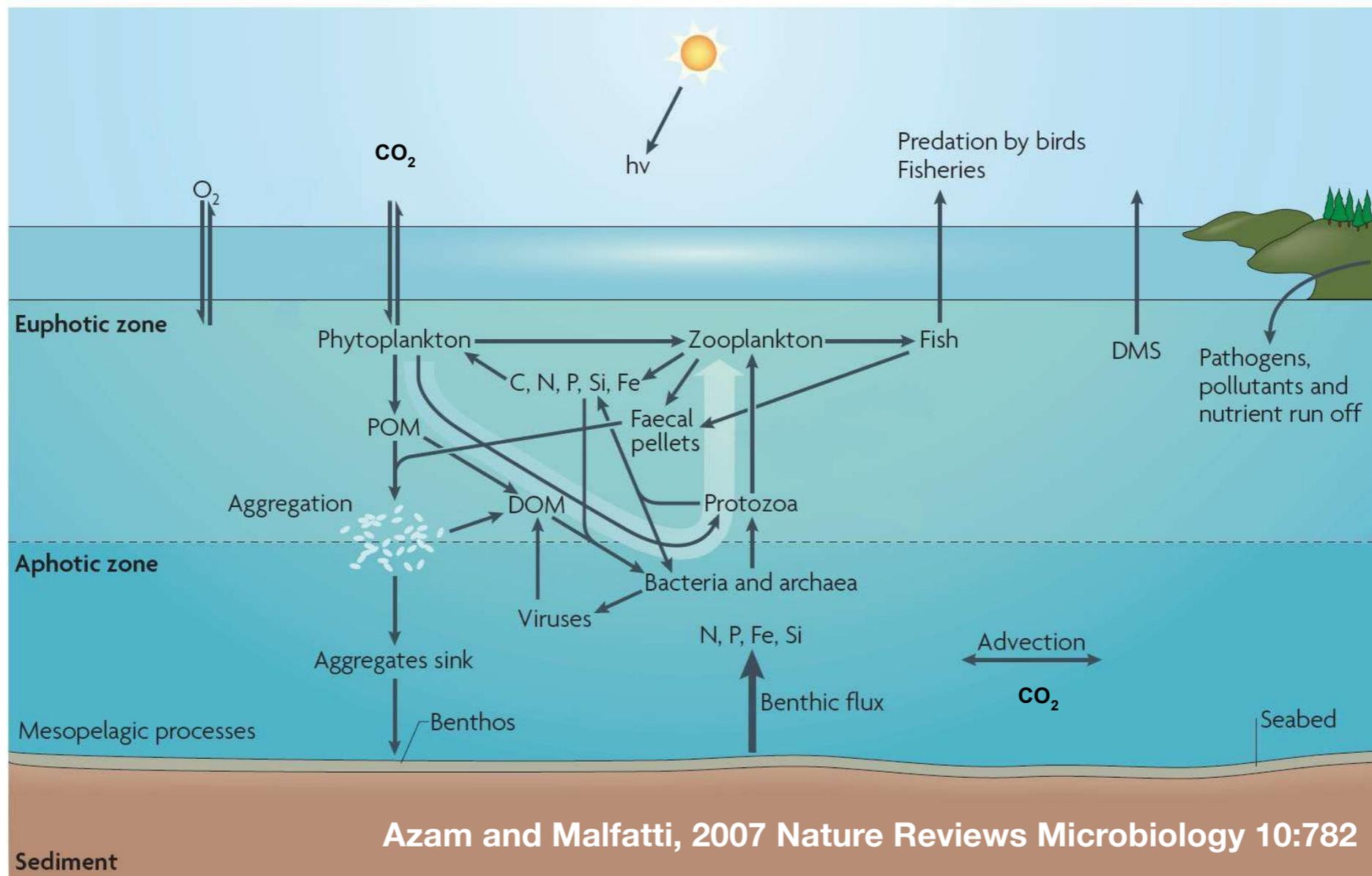


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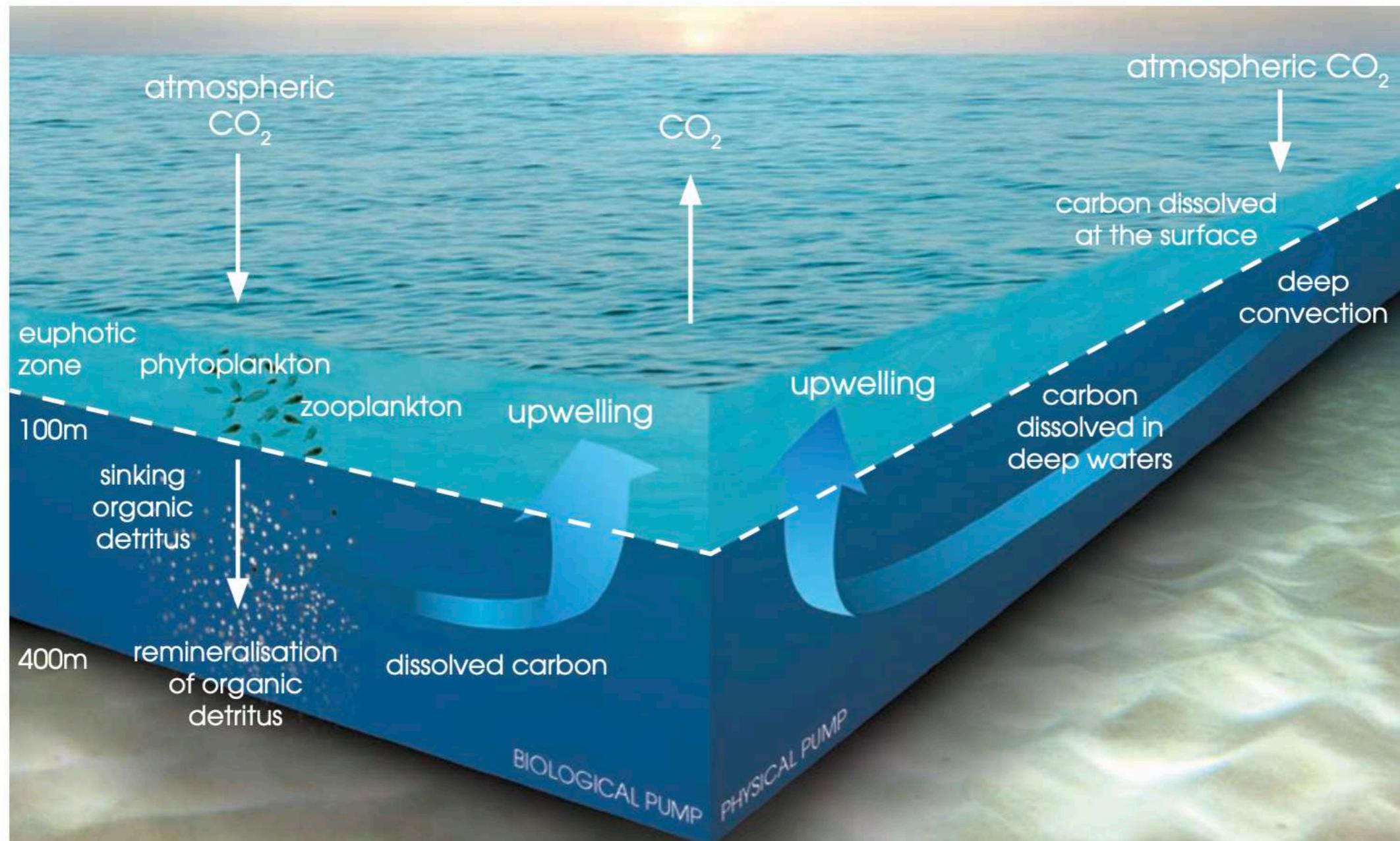


From Genes to Ecosystems

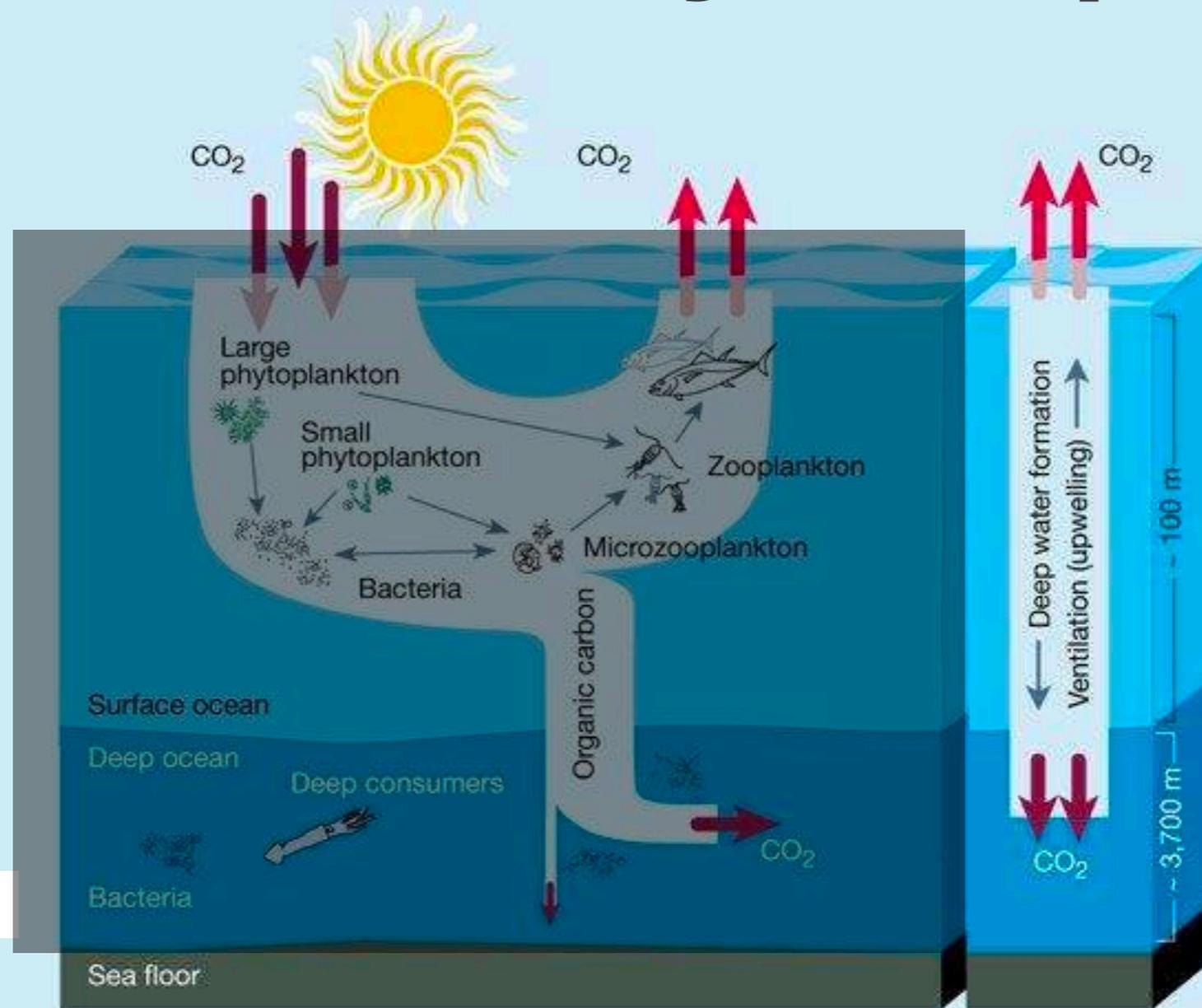
Marine Biogeochemical C Cycle



Biological and physical/solubility pumps



Solubility Pump

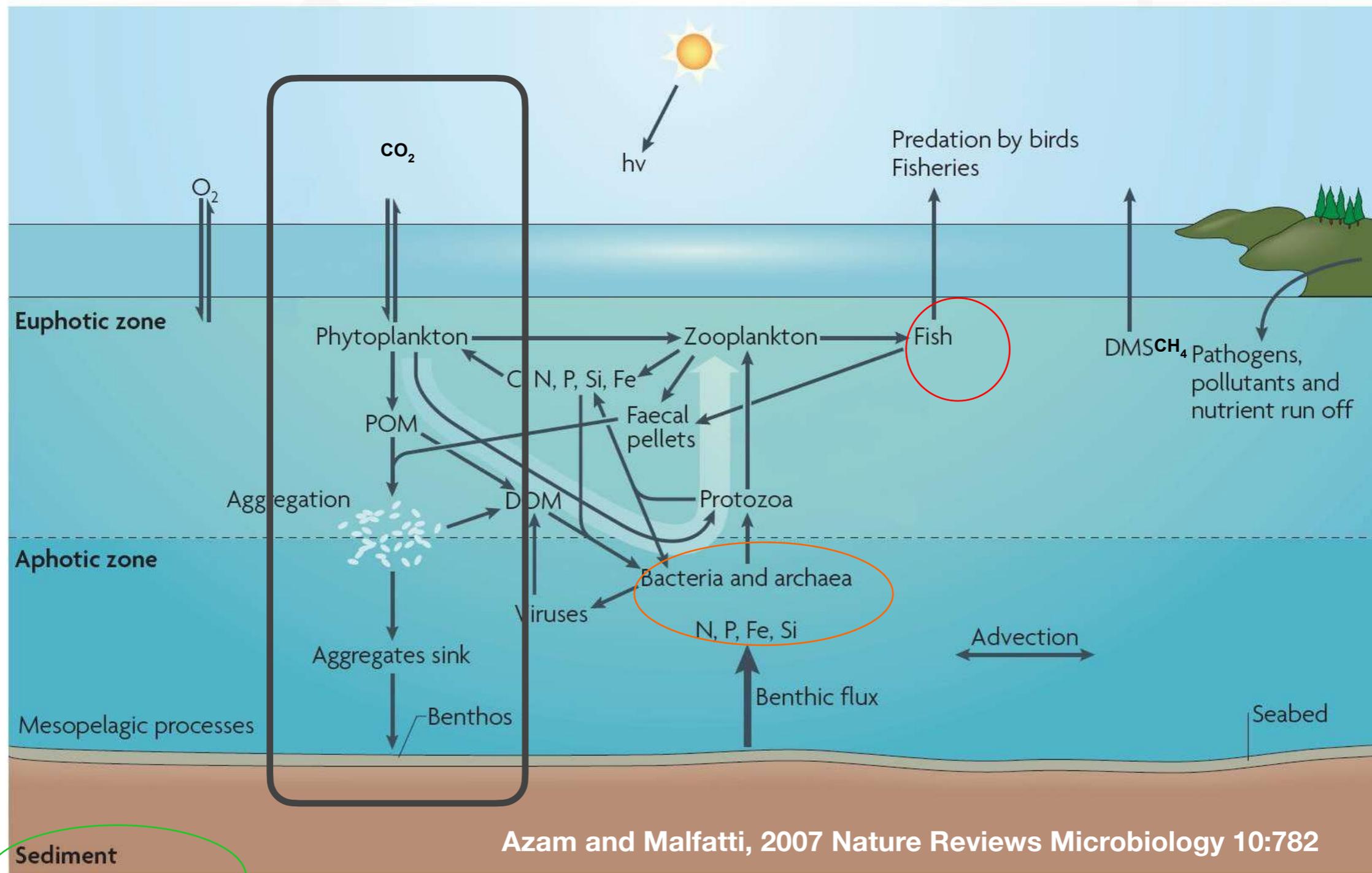


Chisholm, 2000

Solubility pump:

- Cooler water is enriched in CO₂-high latitude regions are sinks for CO₂
- Cooler, CO₂ rich waters sink, deep water formations
- Maintains vertical gradient in CO₂
- Air-sea heat fluxes drive air-sea CO₂ fluxes
- Signature of temperature, salinity and concentrations of dissolved gases

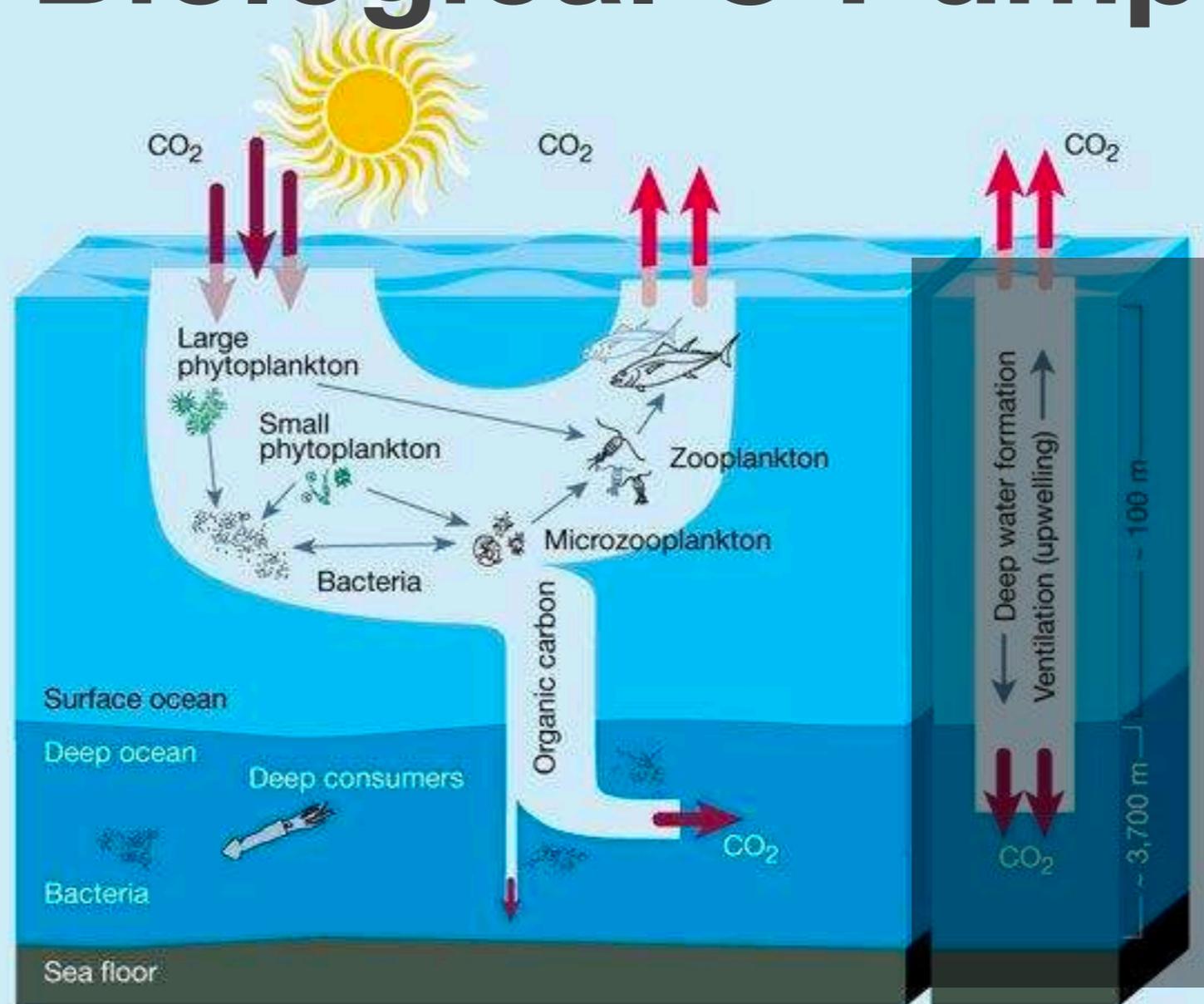
Biological Carbon Pump



Azam and Malfatti, 2007 Nature Reviews Microbiology 10:782

Sediment

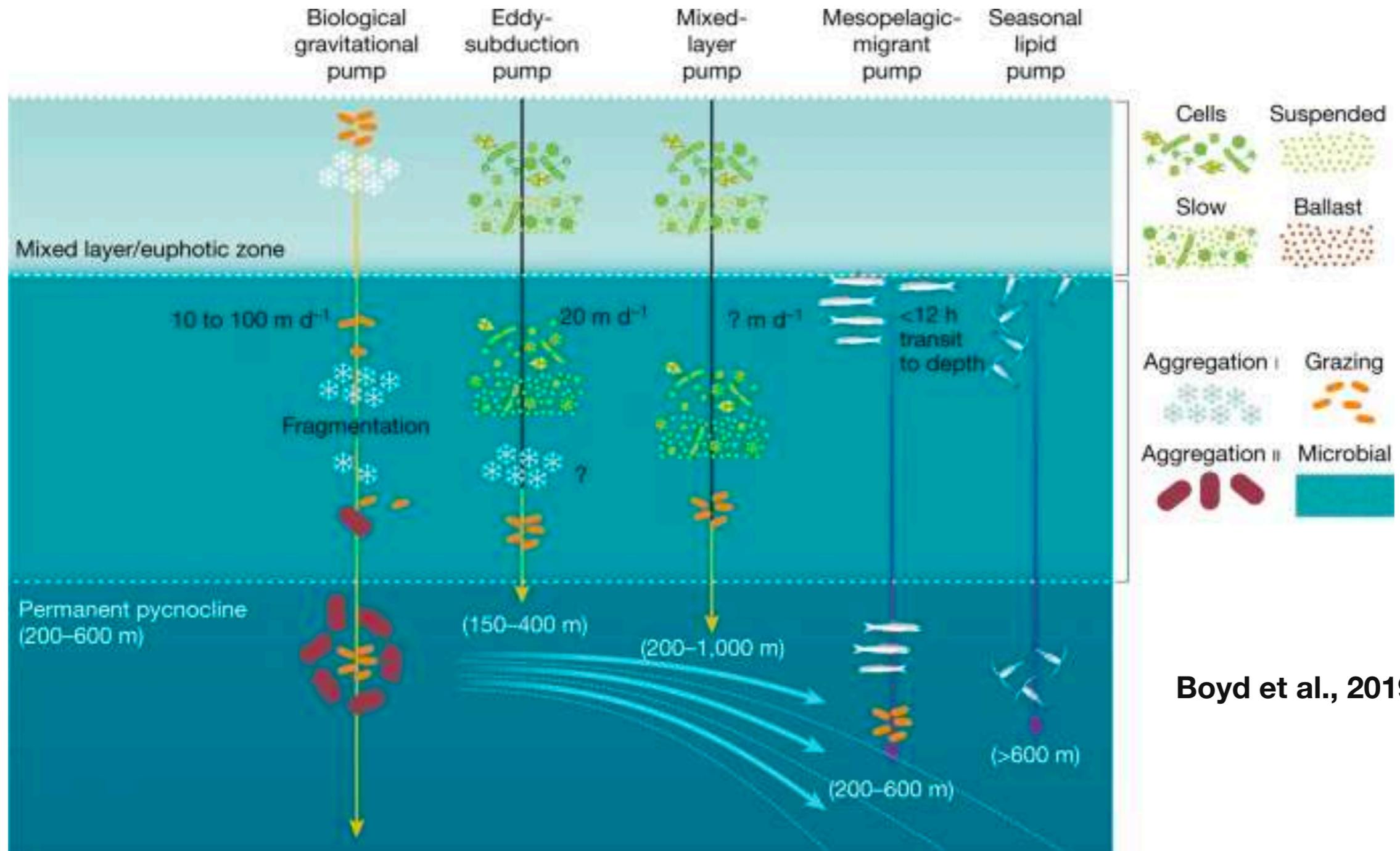
Biological C Pump



Chisholm, 2000

- Productivity transfers CO₂ from solution into organic matter, which in turn is exported to the deeper ocean
- The magnitude of this biological pump can be quantified if two parameters are known: **the amount of surface production and the efficiency of the transport of carbon to depth**
- **Estimates of carbon export** are based on **Redfield ratio**
- For every mole of organic P that is remineralized to PO₄, 106 moles of organic C should be remineralized to CO₂ and 138 moles of O₂ should be consumed → similarity between the stoichiometry of production and respiration suggested similar export efficiency throughout the world's oceans

Interplay between particle characteristics, mode of export (BGP or PIP), delivery depth and larger-scale ocean circulation for a range of pumps



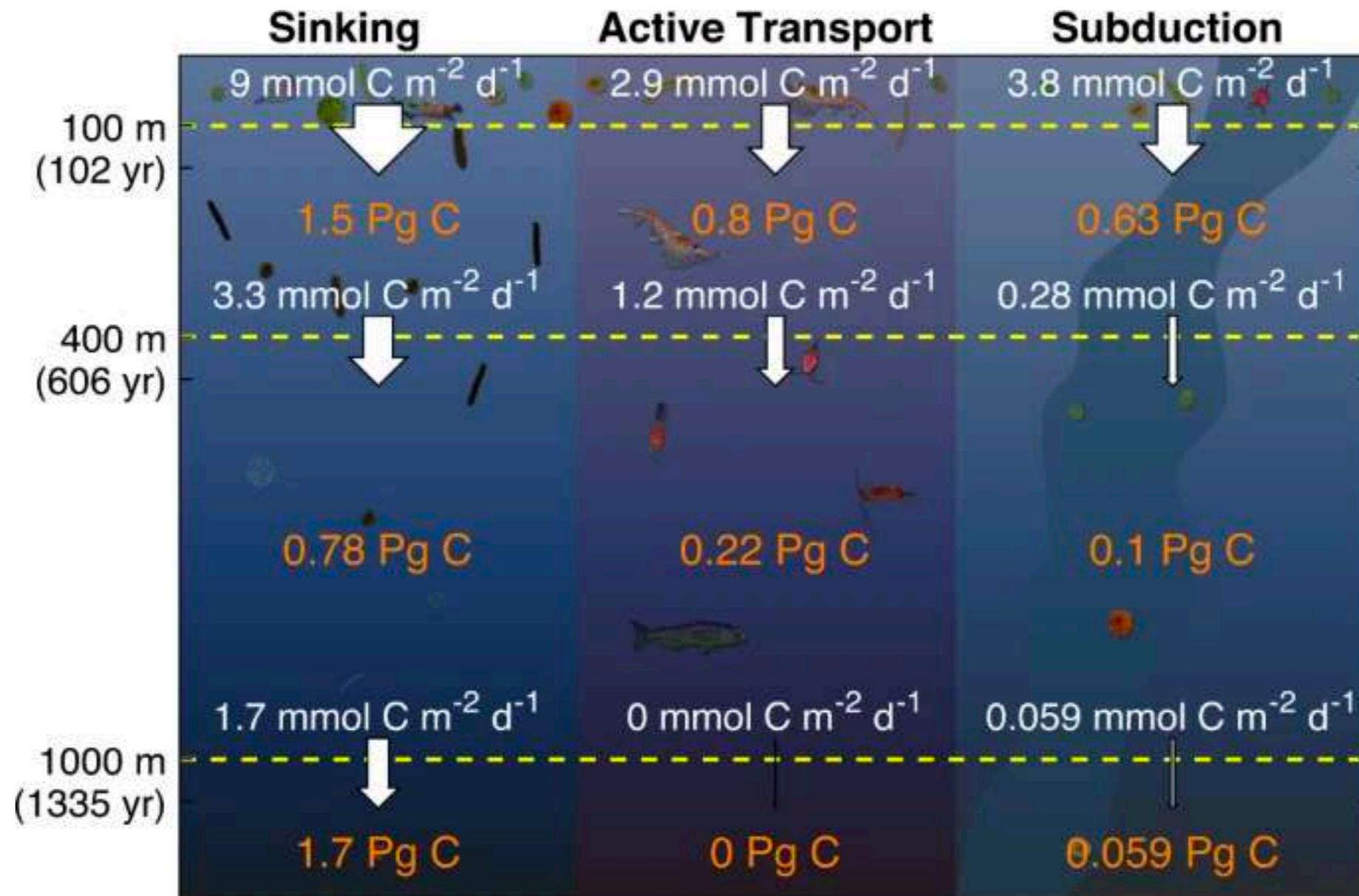
Boyd et al., 2019

In high-latitude regions the **hibernation of copepods** (members of the mesozooplankton) at depths between 600 m and 1,400 m gives rise to a so-called '**seasonal lipid pump**': during winter hibernation, copepods catabolize carbon-rich lipids that they accumulated in the upper layers during summer; in doing so, they shunt carbon (but not nitrogen and phosphorus) below the permanent pycnocline

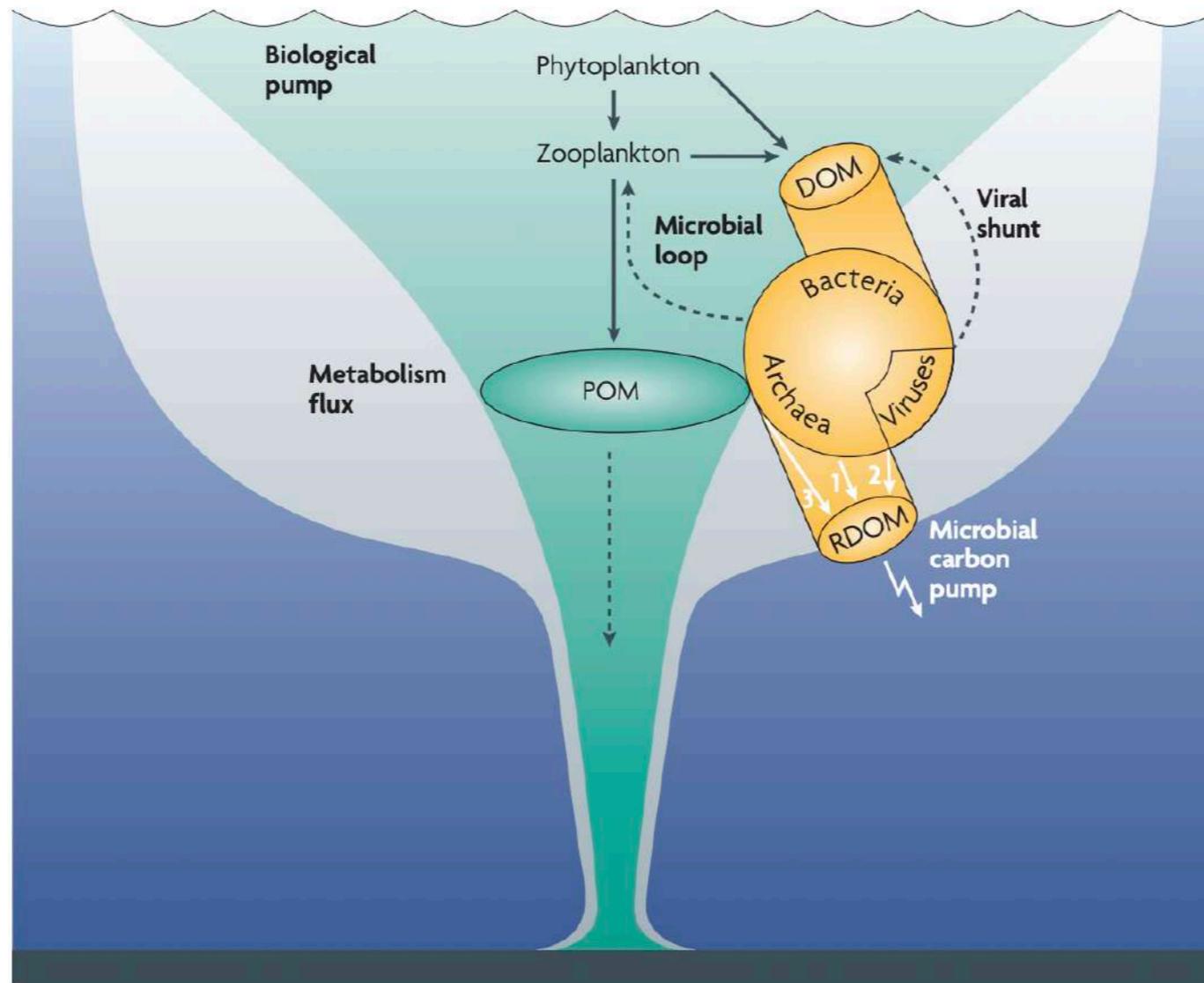
More than just a pump !

BCP likely transports 5–12 Pg C yr⁻¹ into the deep ocean:

(1) sinking particles, (2) active transport by diel vertical migration, and (3) the physical pump (eddy subduction + vertical mixing of particles)



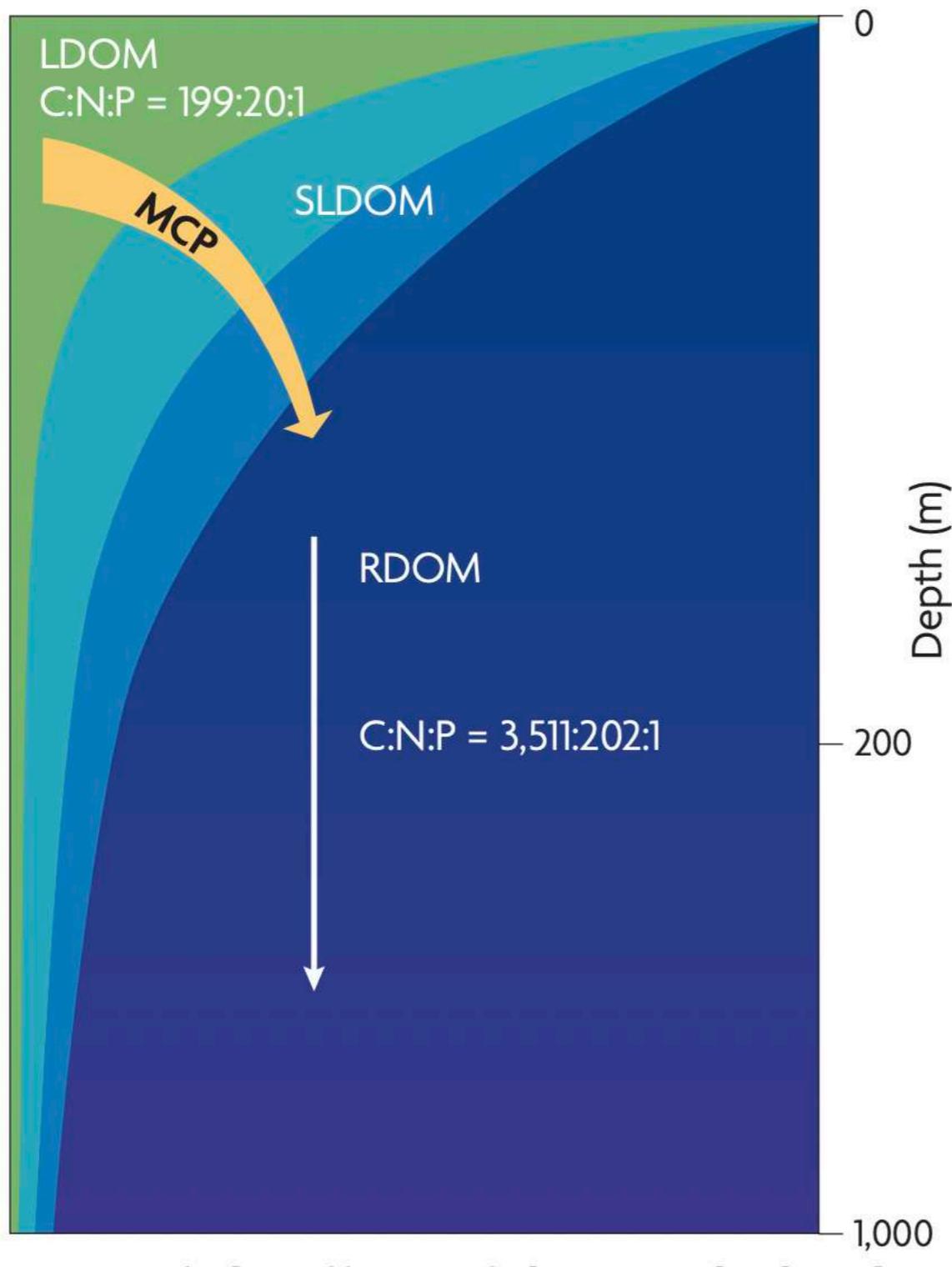
Microbial Carbon Pump



Jiao et al., 2002

Figure 1 | **Major biological processes involved in carbon cycling in the ocean.** The main biological processes are shown. The biological pump is a process whereby CO_2 in the upper ocean is fixed by primary producers and transported to the deep ocean as sinking biogenic particles (particulate organic matter; POM) or as dissolved organic matter (DOM). The microbial loop is a pathway in the aquatic food web whereby DOM is taken up by bacteria and archaea, which are consumed by protists, which are in turn consumed by metazoans (not shown). The viral shunt reflects virus-mediated lysis of microorganisms, which returns the POM to the DOM pool. The proposed microbial carbon pump is a conceptual framework for understanding the role of microbial processes in the production of recalcitrant DOM (RDOM). RDOM can persist in the ocean for millennia and is therefore a reservoir for carbon storage in the ocean. Three major pathways have been identified in the microbial carbon pump: direct exudation of microbial cells during production and proliferation (path 1); viral lysis of microbial cells to release microbial cell wall and cell surface macromolecules (path 2); and POM degradation (path 3). The grey shading roughly indicates the total flux of carbon metabolism in the water column.

The effects of the microbial carbon pump



Recalcitrant DOM

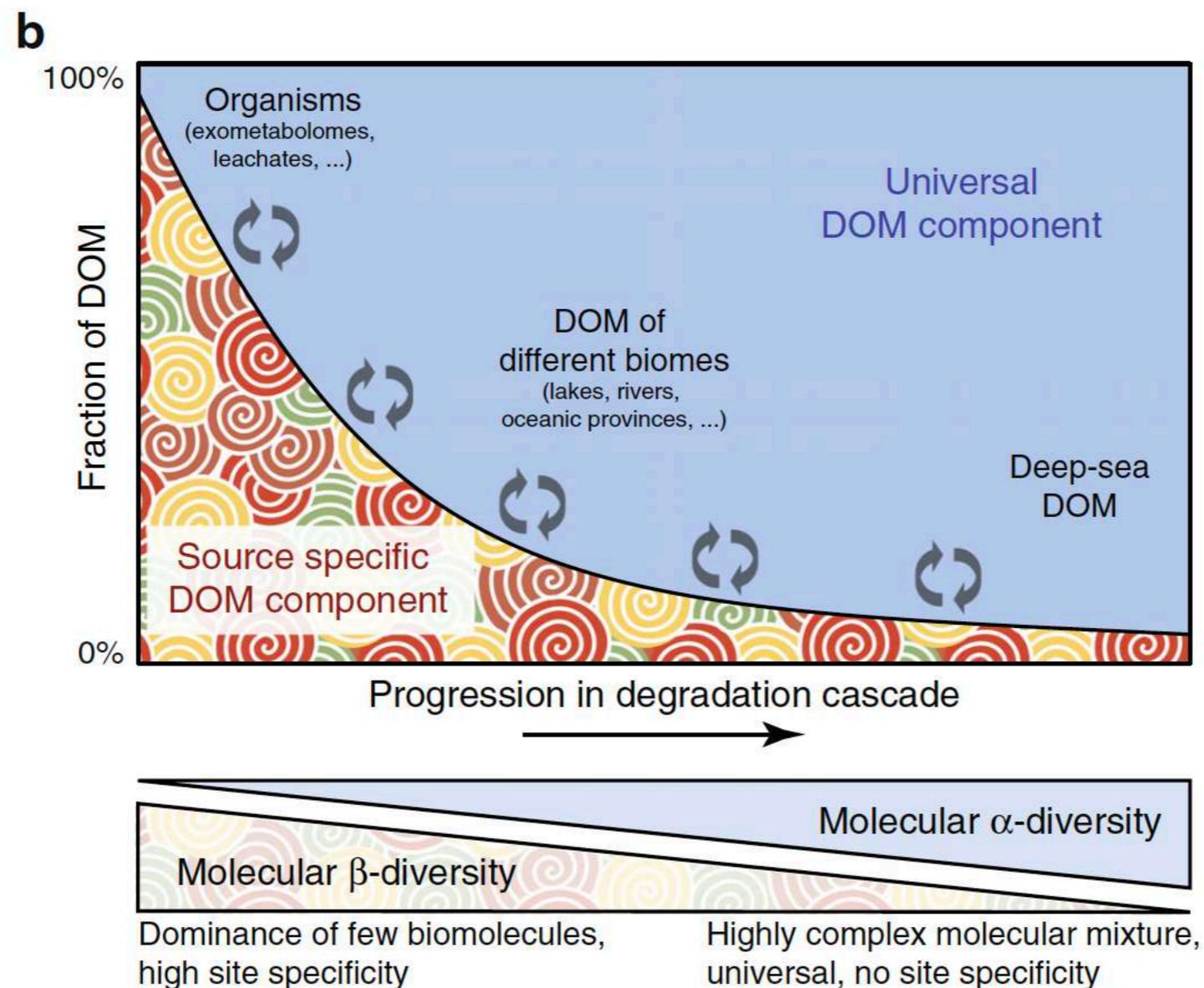
(RDOM). DOM that is resistant to microbial utilization and that can persist in the ocean interior for up to thousands of years. This is the major fraction of DOM found throughout the entire water column, with an inventory of 624 Gt C, accounting for more than 95% of the total dissolved organic carbon in the ocean.

Semi-labile DOM

(SLDOM). DOM that can be used gradually, over months to years. SLDOM is a small fraction of the total ocean DOM (~50 Gt C) and is mainly present in surface waters.

Jiao et al., 2002

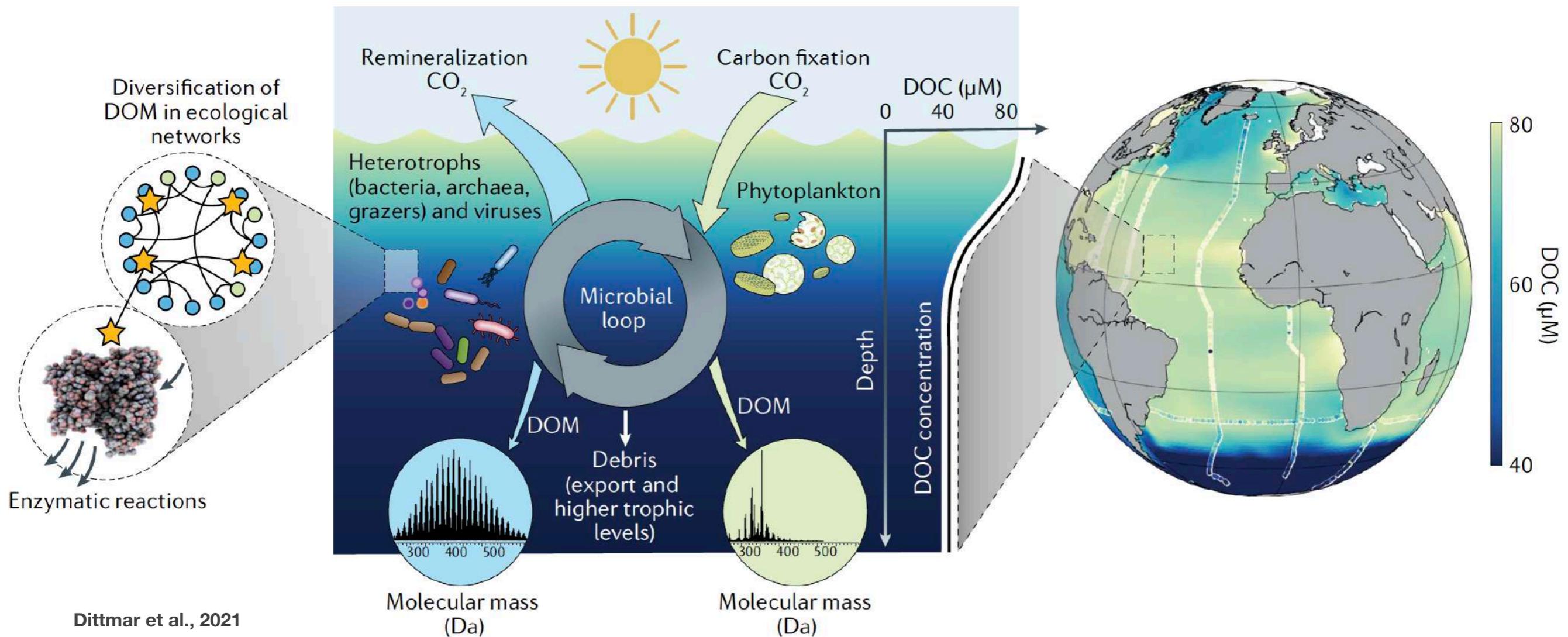
DOM pool



Zark & Dittmar, 2016

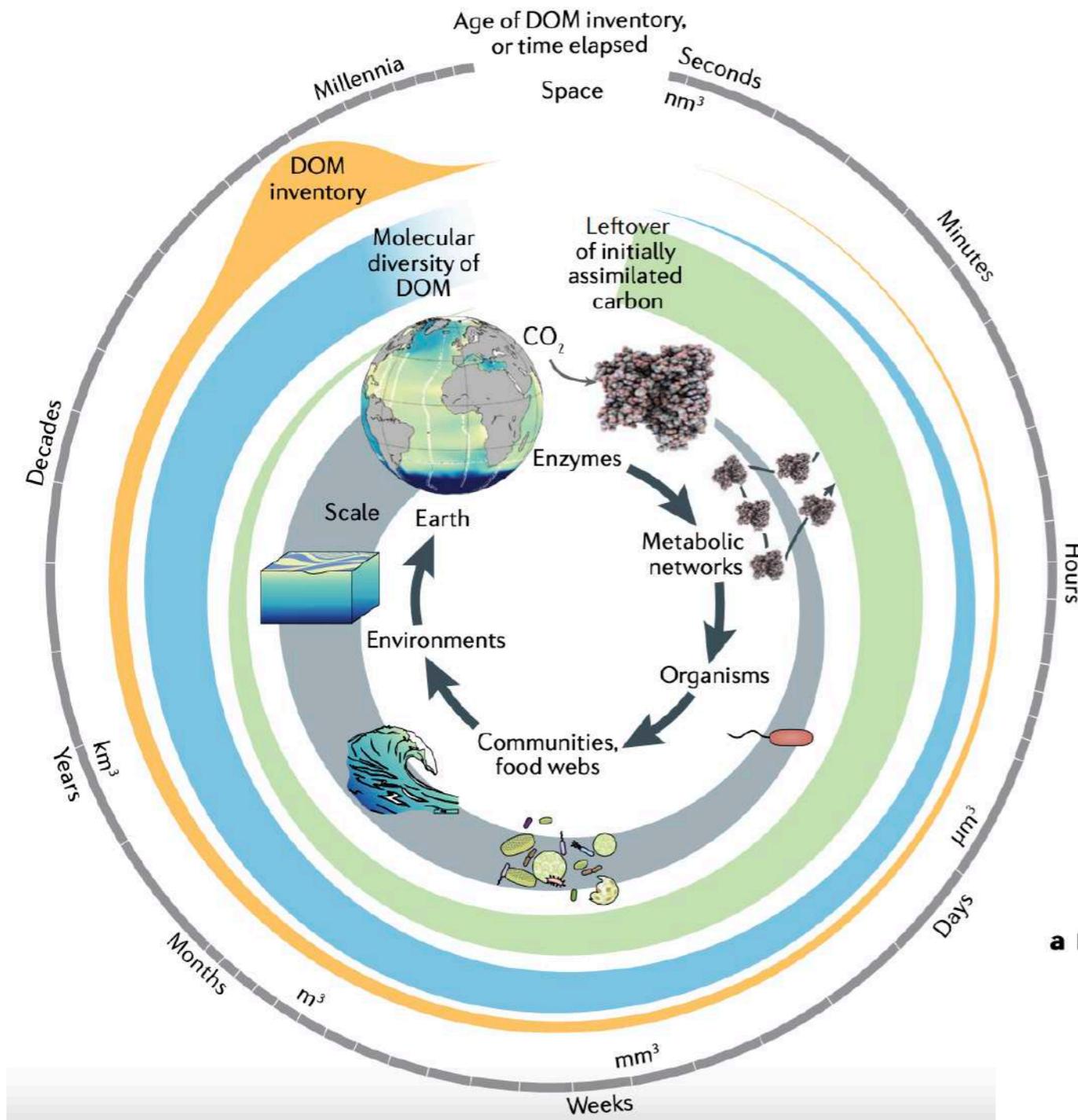
- DOM is broad range of dissolved organic molecules in aquatic systems
- The majority of observable DOM in the ocean has an estimated lifetime of 16,000 years
- Existence of a major component of DOM is molecularly indistinguishable in these diverse samples
- Molecular conformity likely the result of a cascade of degradation processes or common synthetic pathways that ultimately lead to the formation of a universal background, regardless of origin and history of the organic material

Small-scale processes drive global patterns of dissolved organic matter

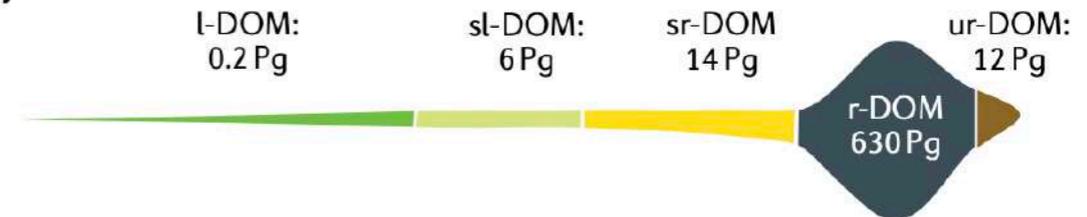


- DOM is about ~660 petagrams of carbon
- 40 petagrams of carbon is turned over every year in this microbial loop
- By ultrahigh-resolution mass spectra, high level molecular diversity of deep ocean DOM vs algae DOM

Formation and degradation of dissolved organic matter across spatial and temporal scales



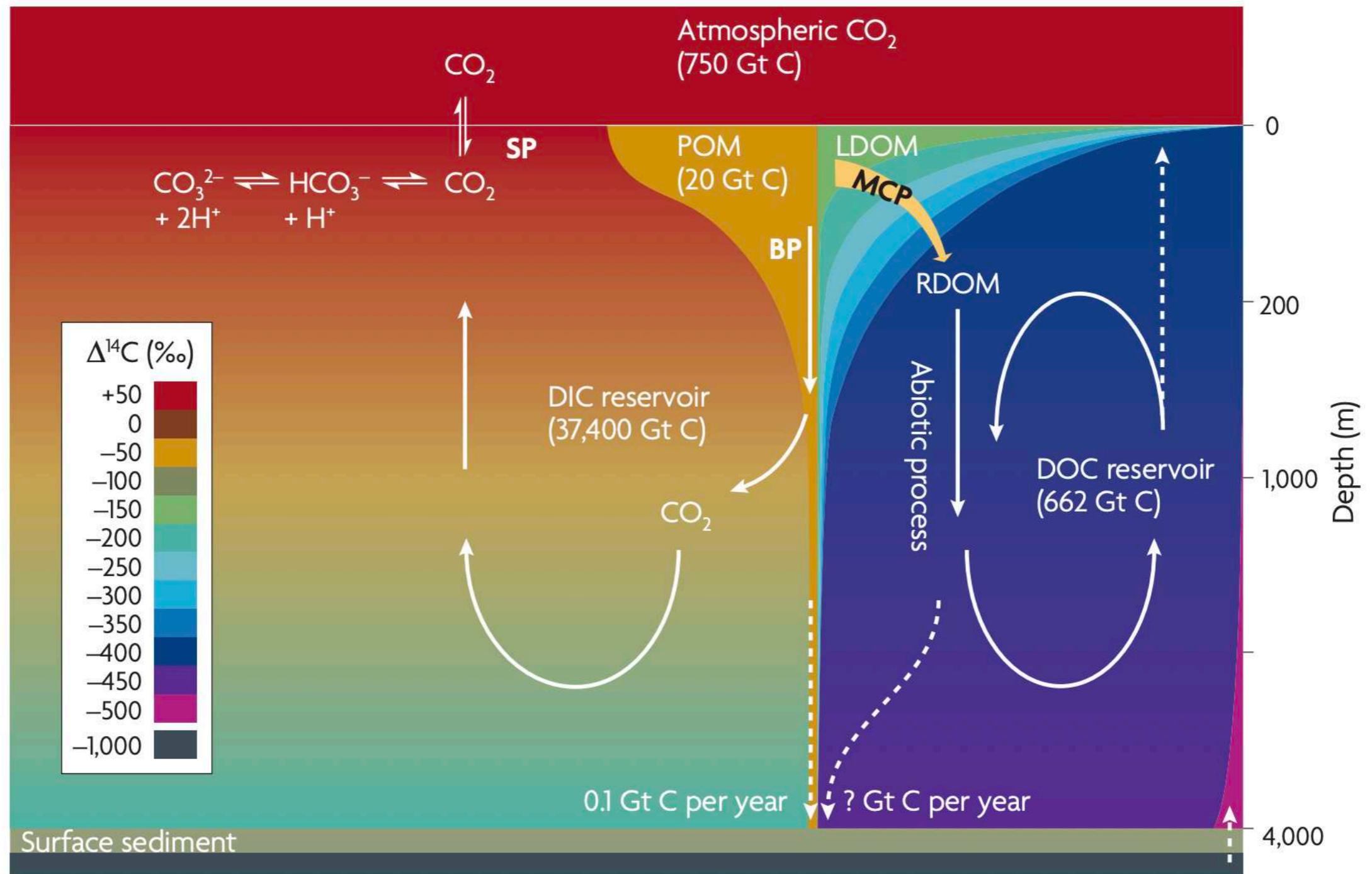
a DOM inventory



Age of DOM inventory or time elapsed



The major mechanisms for formation of oceanic carbon reservoirs

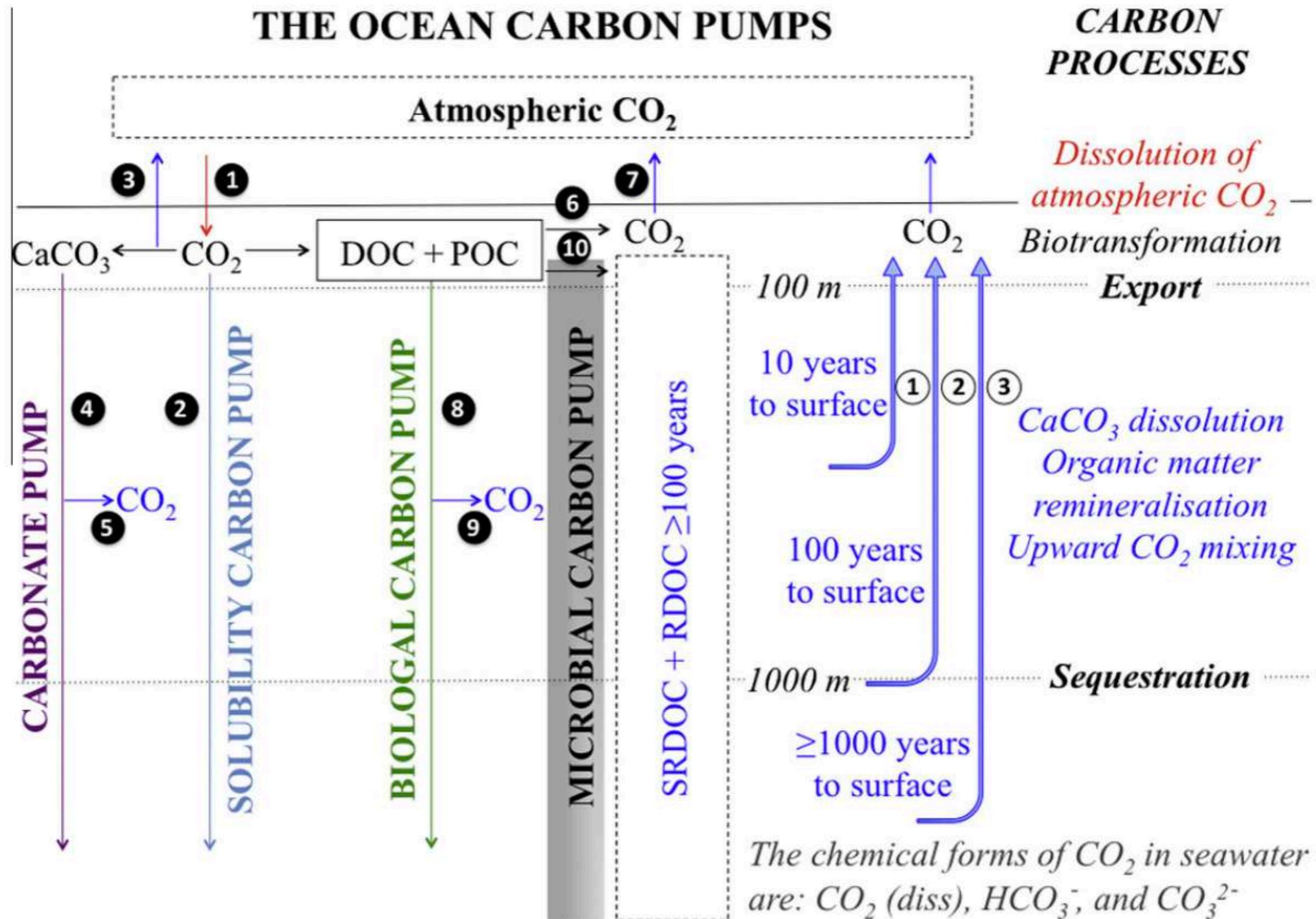


Jiao et al., 2002

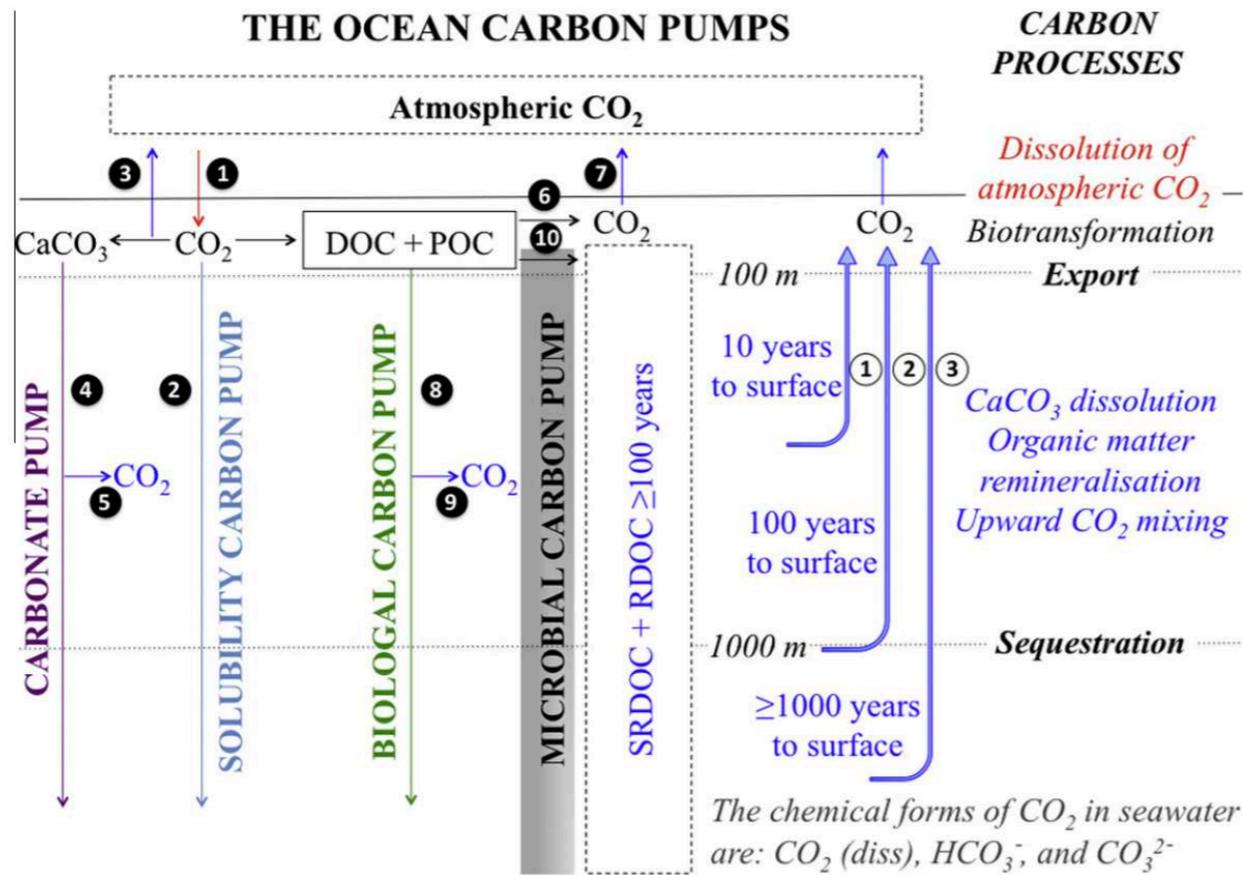
Background colours indicate the rough radiocarbon ages, according to the change in ^{14}C parts per thousand ($\Delta^{14}\text{C}$ ‰) values

The three vertical ocean carbon pumps, the DOC fractions and the Microbial Carbon Pump

L. Legendre et al. / Progress in Oceanography xxx (2015) xxx–xxx



Legendre, Louis, et al. "The microbial carbon pump concept: Potential biogeochemical significance in the globally changing ocean." *Progress in Oceanography* 134 (2015): 432-450.



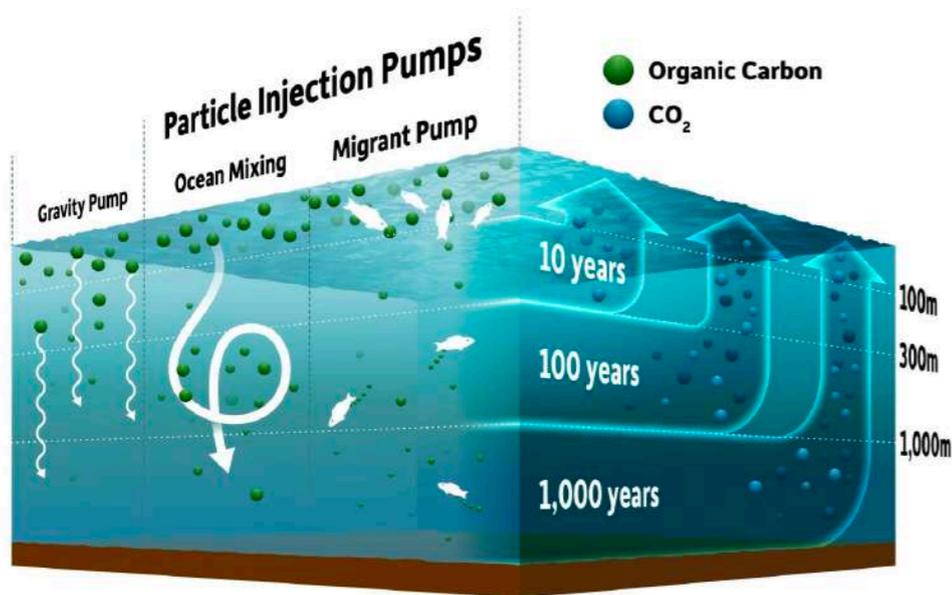
Three vertical carbon pumps:

the **Carbonate Pump**, i.e. bio-precipitation of CaCO_3 in the upper water column (which is accompanied by the release of CO_2 ③), followed by sinking of bio-mineral particles to depth where their carbon is sequestered ④;

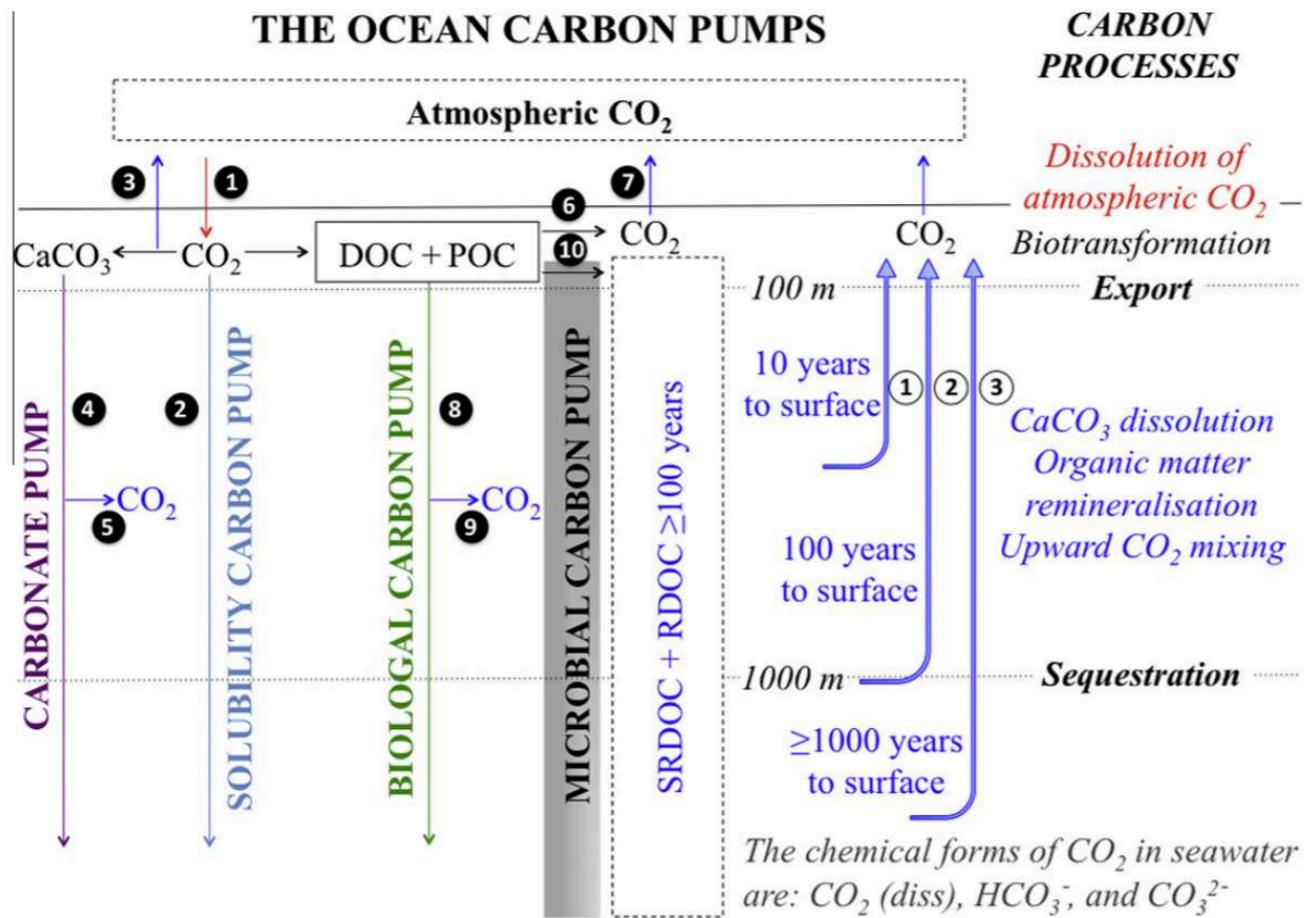
the **Solubility Pump**, i.e. dissolution of atmospheric CO_2 in surface waters ①, followed by deep mixing of the CO_2 -rich water and sequestration ②;

and the **Biological Carbon Pump**, i.e. photosynthetic uptake of carbon by phytoplankton and its transformation by the food web in the euphotic zone, including respiration ⑥ and loss of to the atmosphere ⑦, followed by transfer of organic carbon into deep waters where it is sequestered ⑧.

Boyd et al., 2019

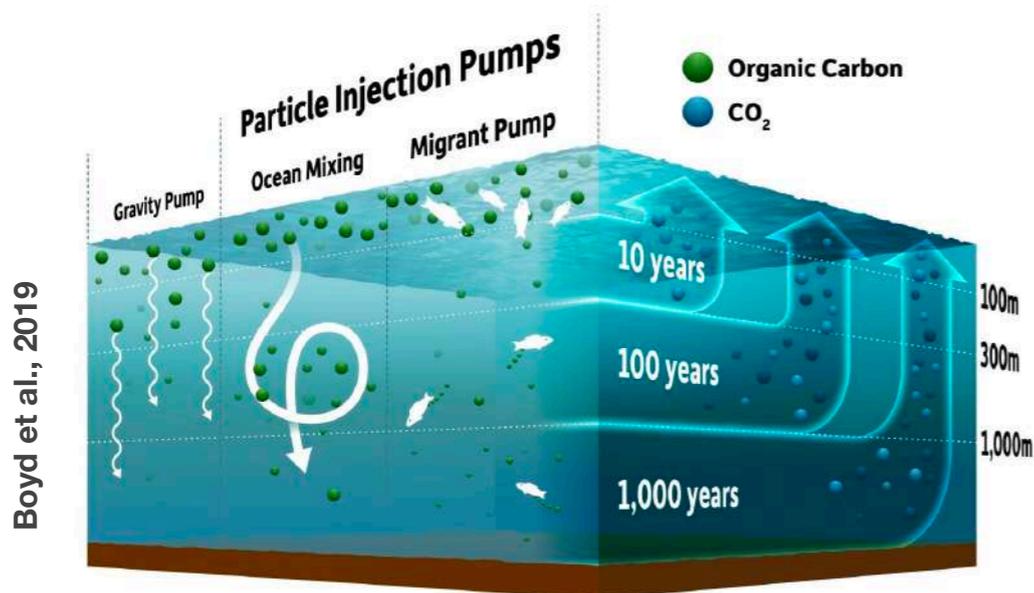


Total dissolved inorganic carbon: CT



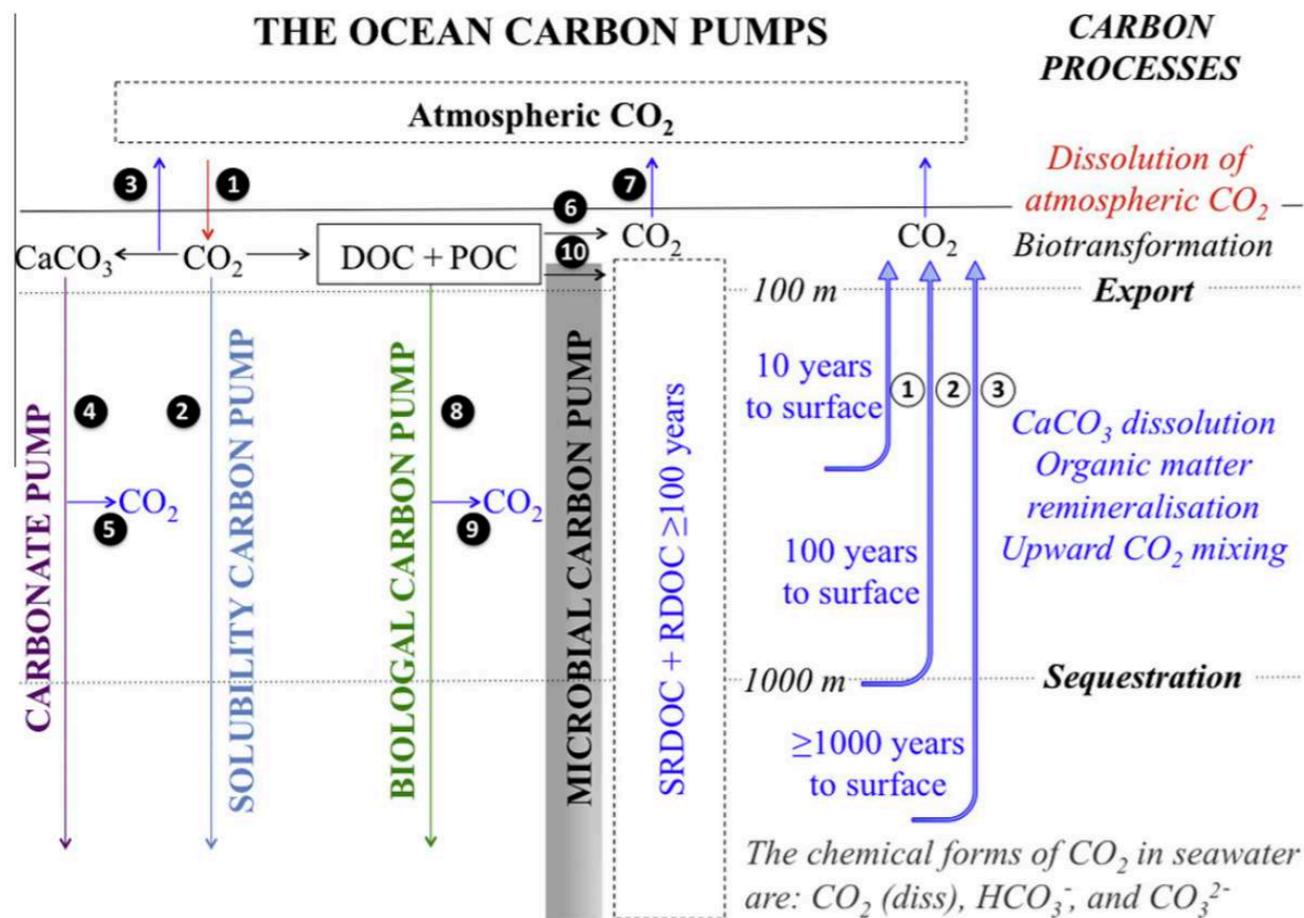
By maintaining the vertical gradient in CT, the carbon pumps regulate the exchange of CO₂ between the atmosphere and the ocean.

Inorganic and organic carbon that is transferred below the euphotic zone or the seasonal surface mixed layer (represented here by the 100 m depth horizon) is considered to be exported, and the fraction of exported carbon that does not return to surface waters and the atmosphere within 100 years is considered to be sequestered, which is the case for carbon that reaches the average depth of ca. 1000 m in the ocean.



During the downward transit from 100 to 1000 m, CO₂ is released in the water column by dissolution of part of the sinking CaCO₃ ⑤ and remineralisation of part of the organic carbon that is transferred to depth ⑨.

L. Legendre et al./Progress in Oceanography xxx (2015) xxx–xxx



The CO₂ that “leaks” (i.e. escapes) from the three carbon pumps above the depth of sequestration may return to the surface by upward mixing, where it can be exchanged with the atmosphere (① to ③).

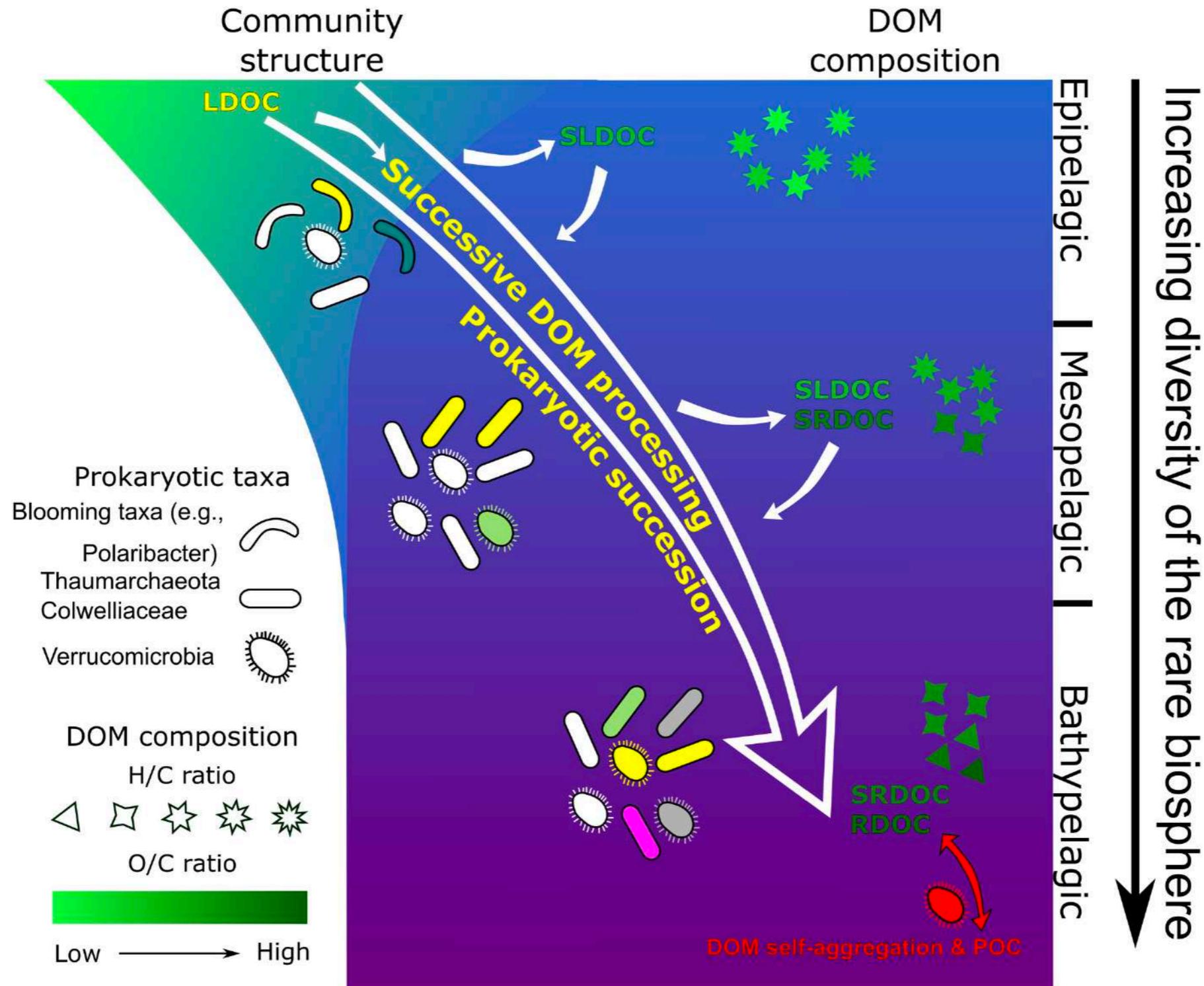
Below the average ca. 1000 m depth, carbon is either entrained in the **deep-ocean circulation**, which has a characteristic turnover time of ca. 1000 years, or **buried in sediments** where it enters cycles that last millions of years.

The production of RDOC and SRDOC with a lifetime >100 years (i.e. DOC > 100 years, from POC and less refractory DOC, i.e. SLDOC and SRDOC), presumably by microbial activity, will sequester ocean carbon because their lifetimes are >100 years ⑩.

The production of DOC > 100 years results from MCP processes, which maintain the large gradient that exists between short-lived and long-lived DOC.

Production of DOC > 100 years is thought to take place mainly in surface waters, but it may occur at all depths; the resulting RDOC is distributed over all oceans depths.

Deep ocean microbial communities produce more stable dissolved organic matter through the succession of rare prokaryotes



LaBrie et al., 2022

The successive transformation of labile DOM compounds to produce increasingly more RDOC was concomitant to the succession of prokaryotic taxa that was more efficient in deeper communities