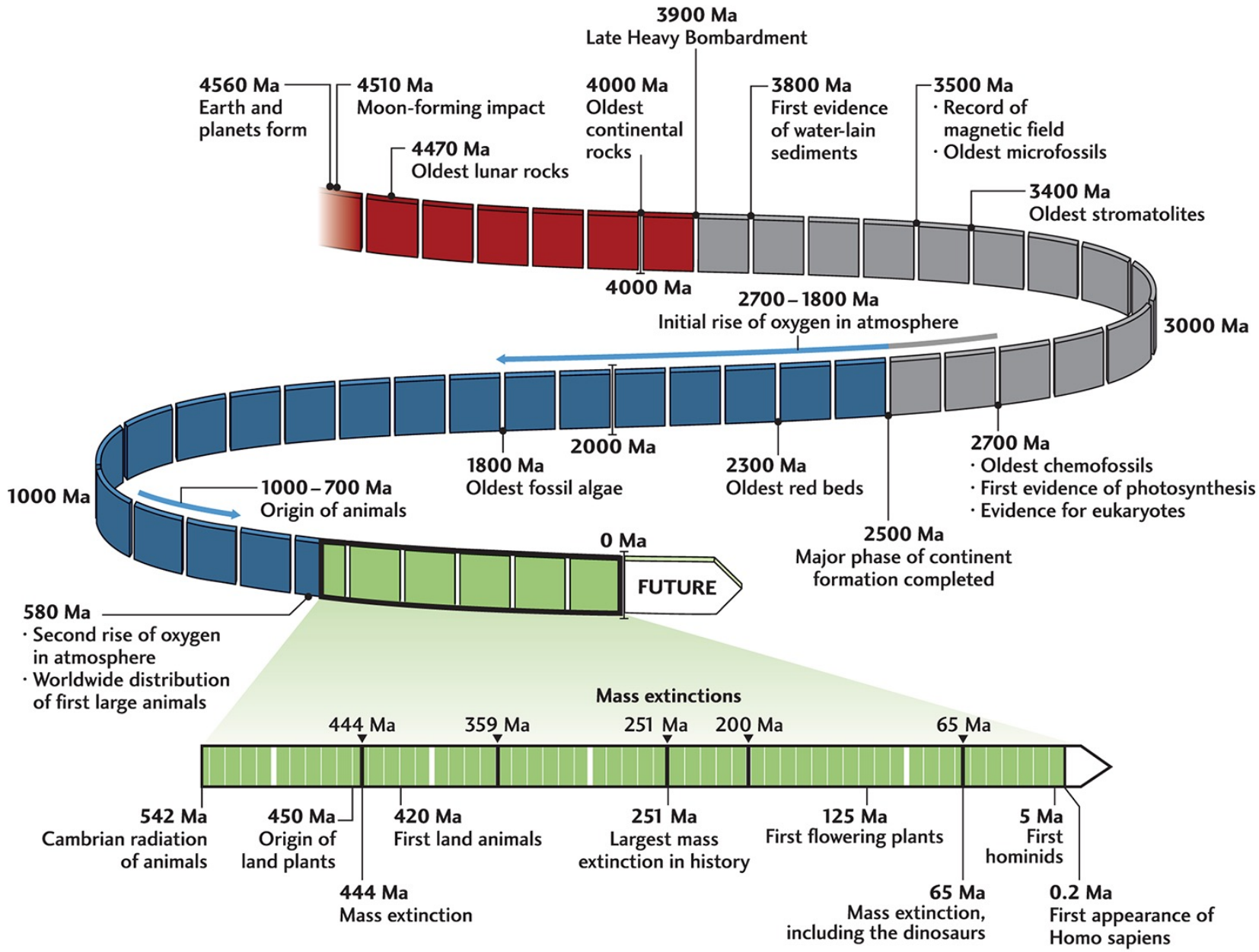
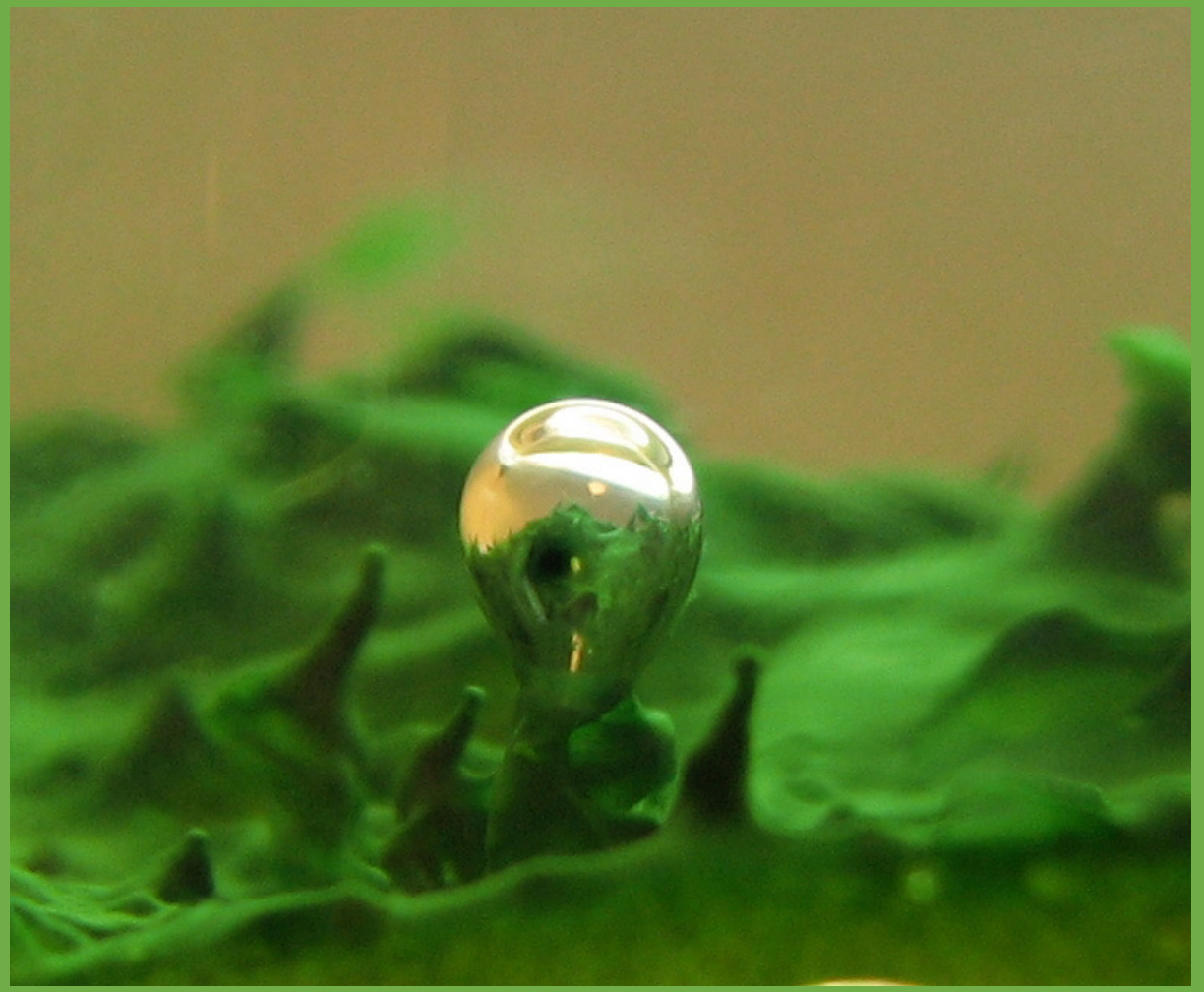
Microbial and Environmental Co-Evolution

- Redox and photosynthesis
- Redox processes in modern environments
- Geochemical and geologic evidence for redox changes
- Geologic evidence for biological evolution
- Molecular and fossil evidence for the evolution of oxygen-producing microbes
- Microbial processes that make carbonate rocks

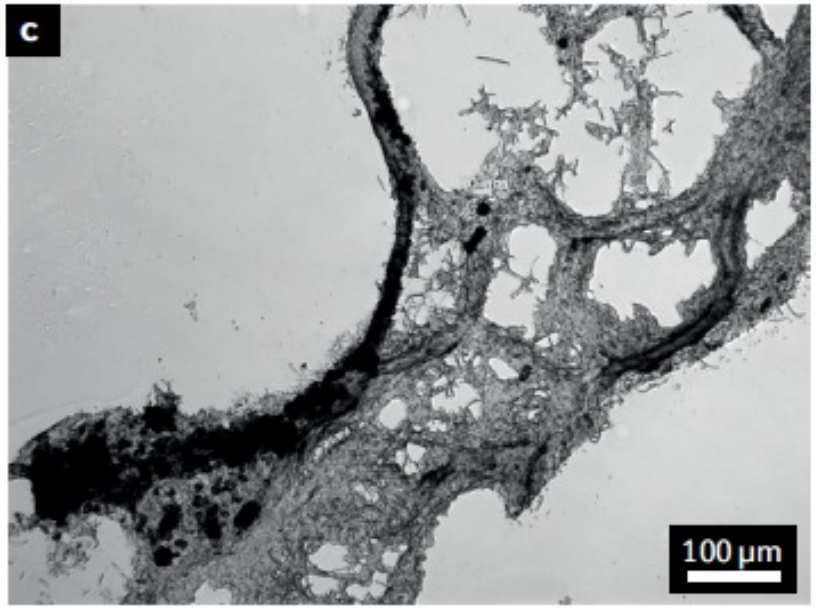


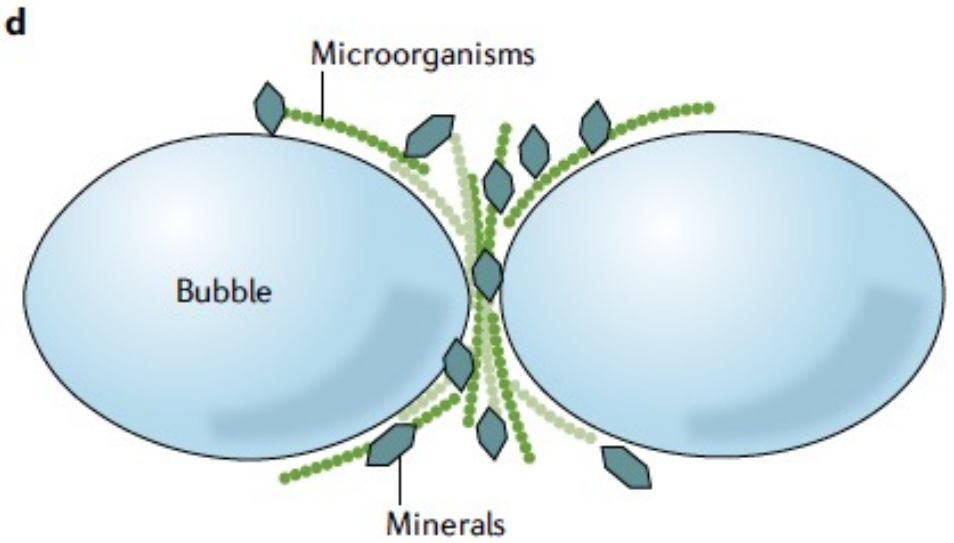
Cyanobacteria Invented Oxygenic Photosynthesis (Yes, But When?)



$H_2O + CO_2 \rightarrow CH_2O + O_2$

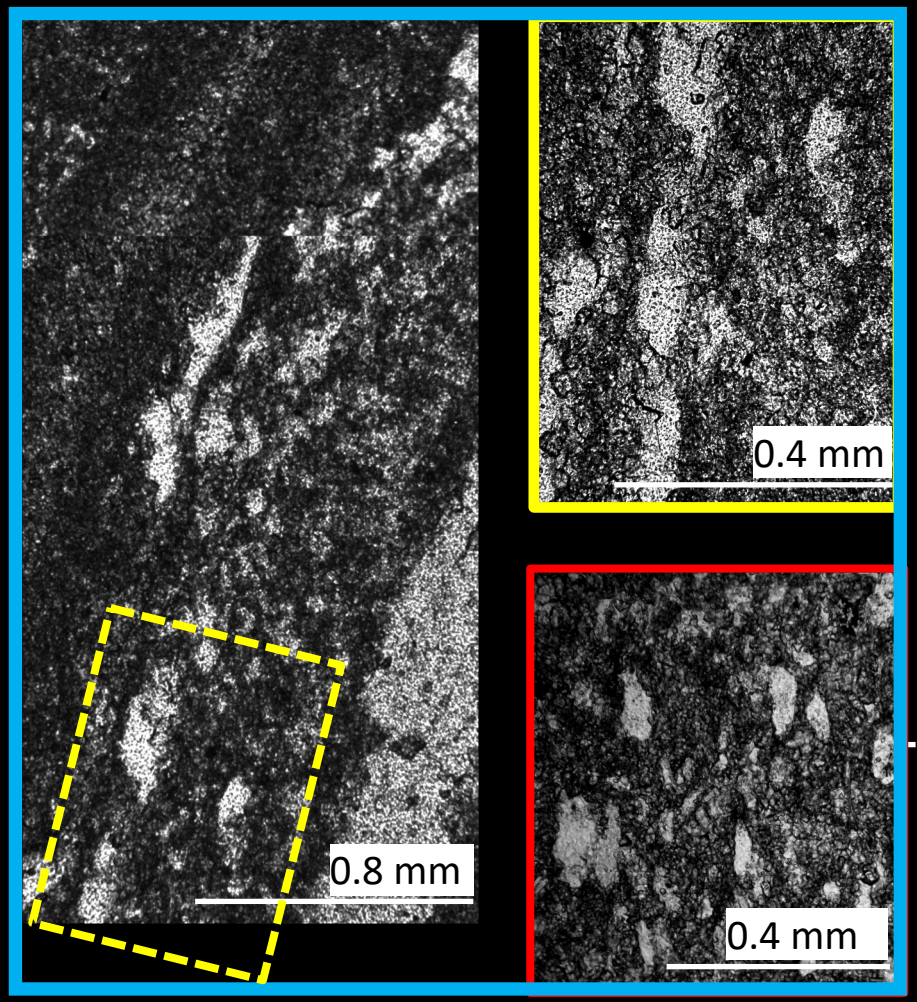
Cyanobacterial Mats Produce and Trap Bubbles



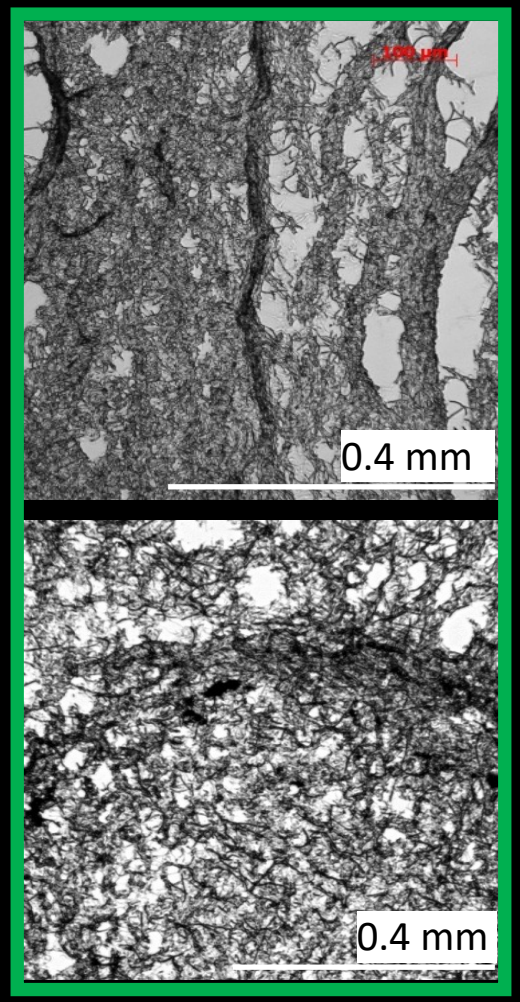


(Bosak et al., 2021)

Fine Carbonate Laminae of Archean Stromatolites: Chemical and Biological Changes?



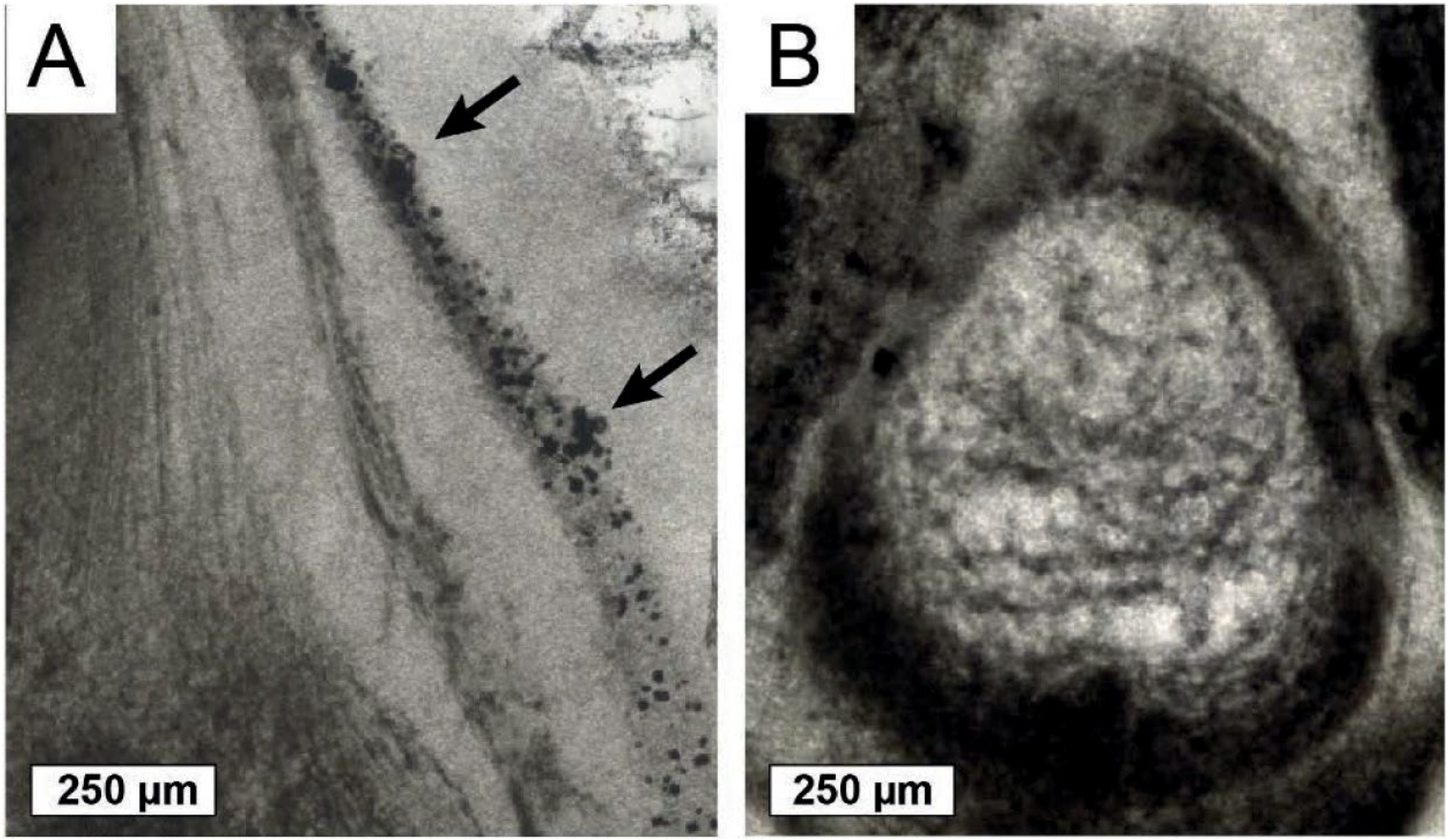
2. 98 BILLION YEARS OLD



MODERN

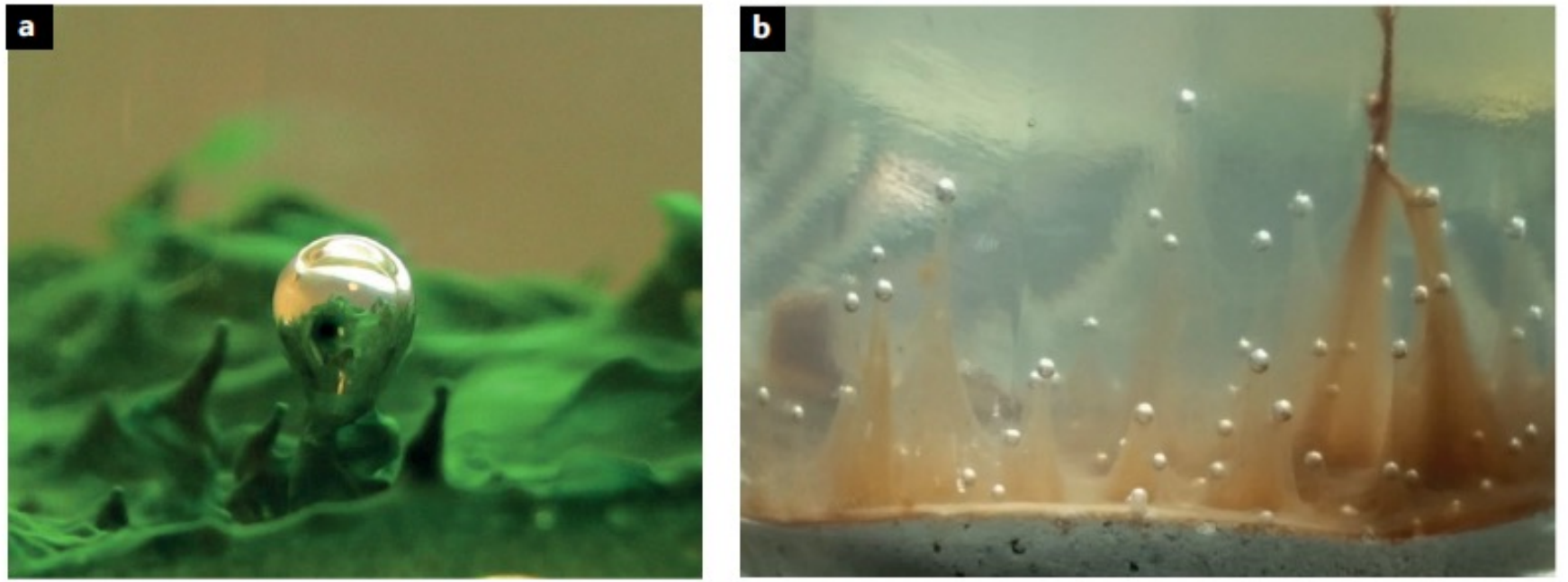
(Bosak et al., 2009; 2010; Bosak, Knoll, Petroff, *Annu Rev Earth Planet Sci*, 2013)

Possible Bubbles in 2.7 Ga Stromatolites from the Hartbeesfontein Basin, Ventersdorp Supergroup, South Africa



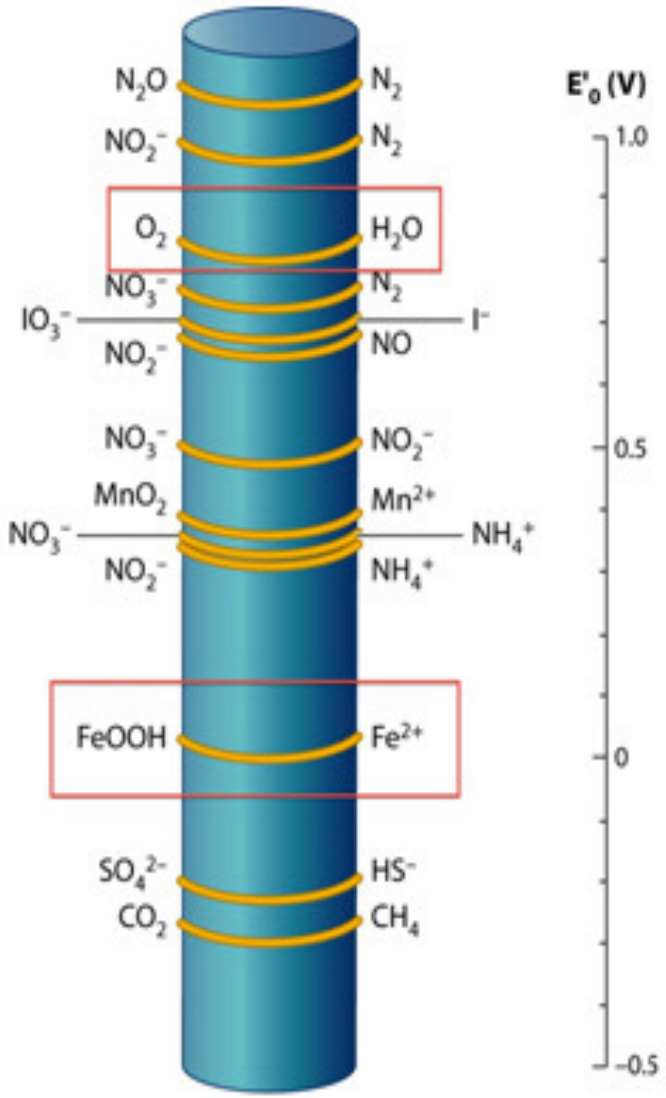
(Wilmeth et al., 2019)

But Microbial Mats Can Bind Bubbles in the Absence of O_2



(Bosak et al., 2021)

Photosynthetic Redox Centers

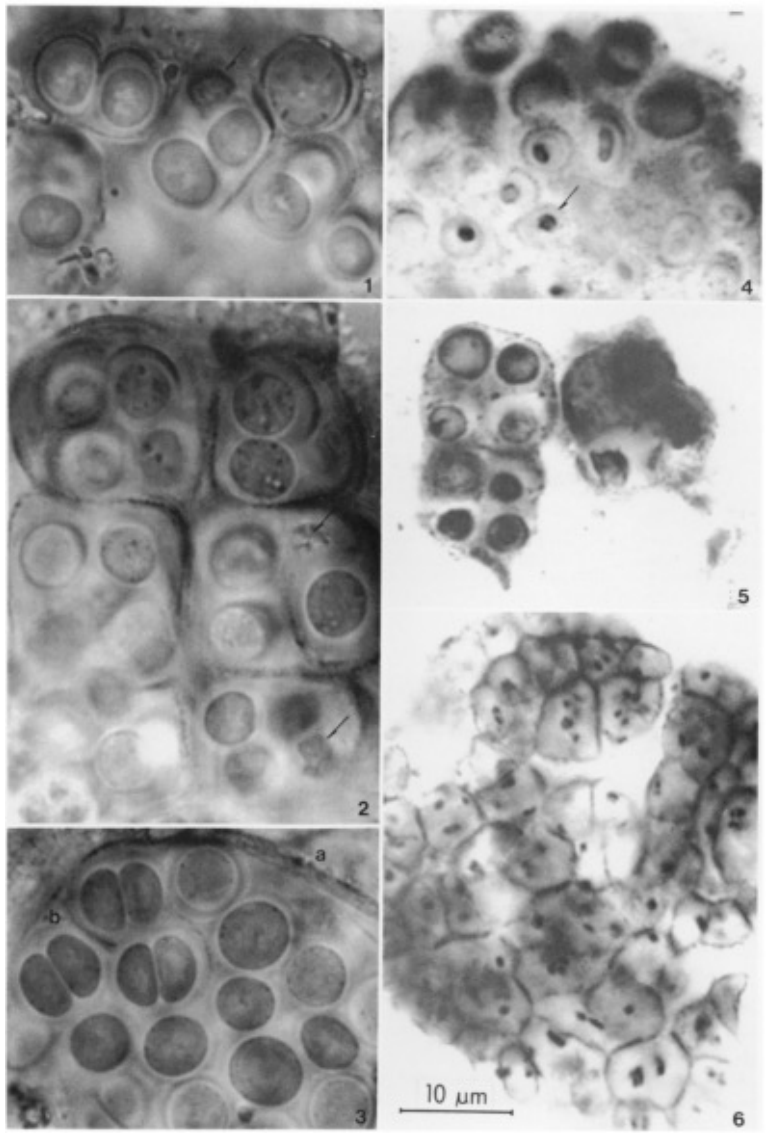


$P680^+/P680$

$P870^+/P870$

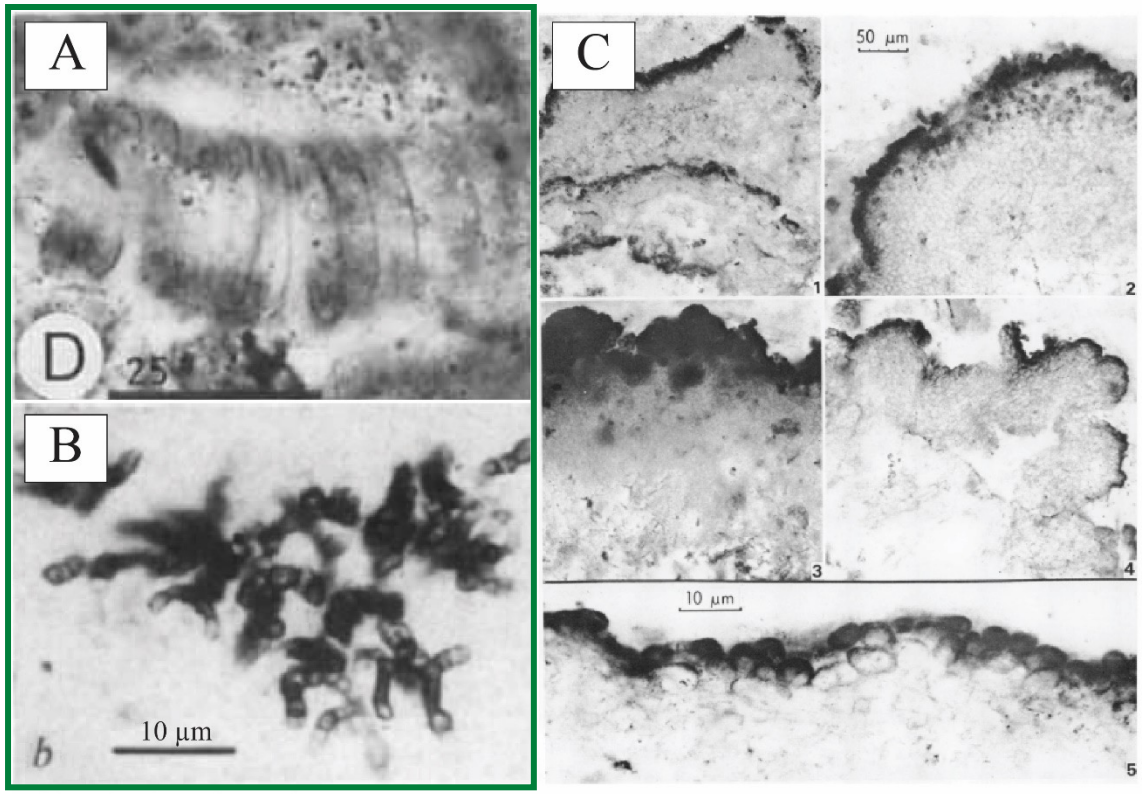
$E' = -\Delta G'/nF$

2 Ga Cyanobacterial Fossils



(Golubic and Hofmann, 1969)

Fossil Calibrations

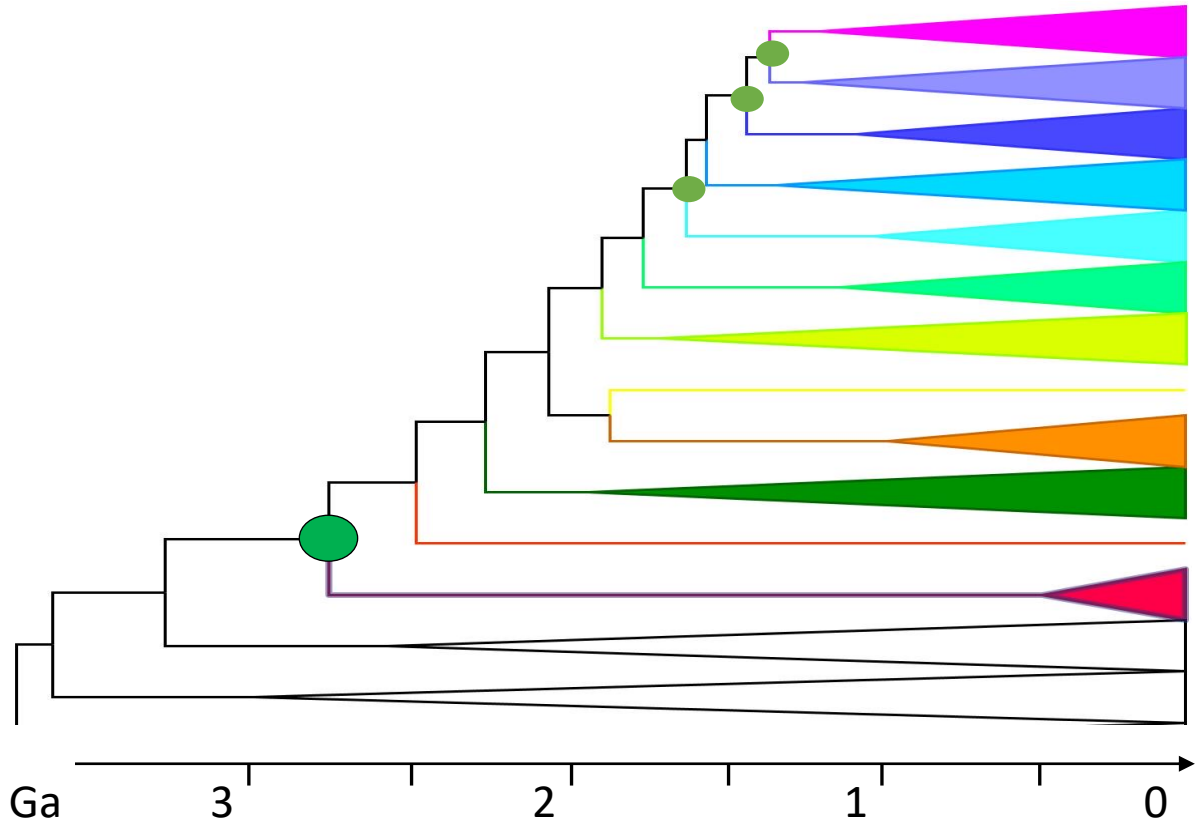


A) *Obruchevella* ~1500 Ma (image from Knoll and Ohta, 1988)

B) *E*ndolithic cyanobacteria ~800 Ma (image from Knoll et al., 1986), some suggested at 1700 Ma

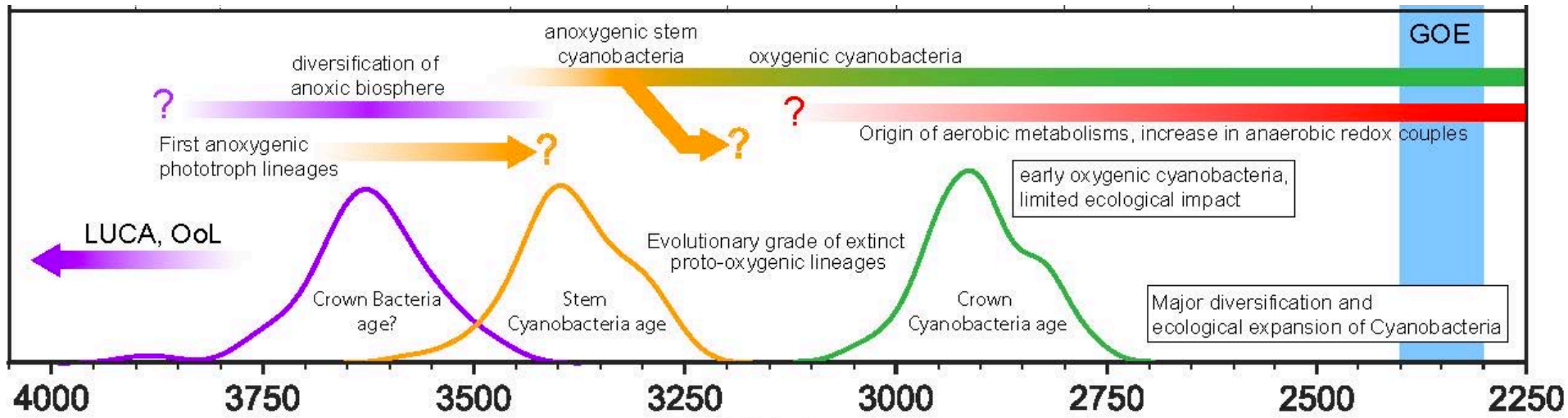
C) *Eoentophysalis* ~2000 Ma (image from Hofmann, 1976)

Molecular Clock Models



(Moore et al., *Frontiers Micro*, 2019; Fournier et al., *Proc Roy Soc B*, 2021)

The Phylum Cyanobacteria Predates the GOE

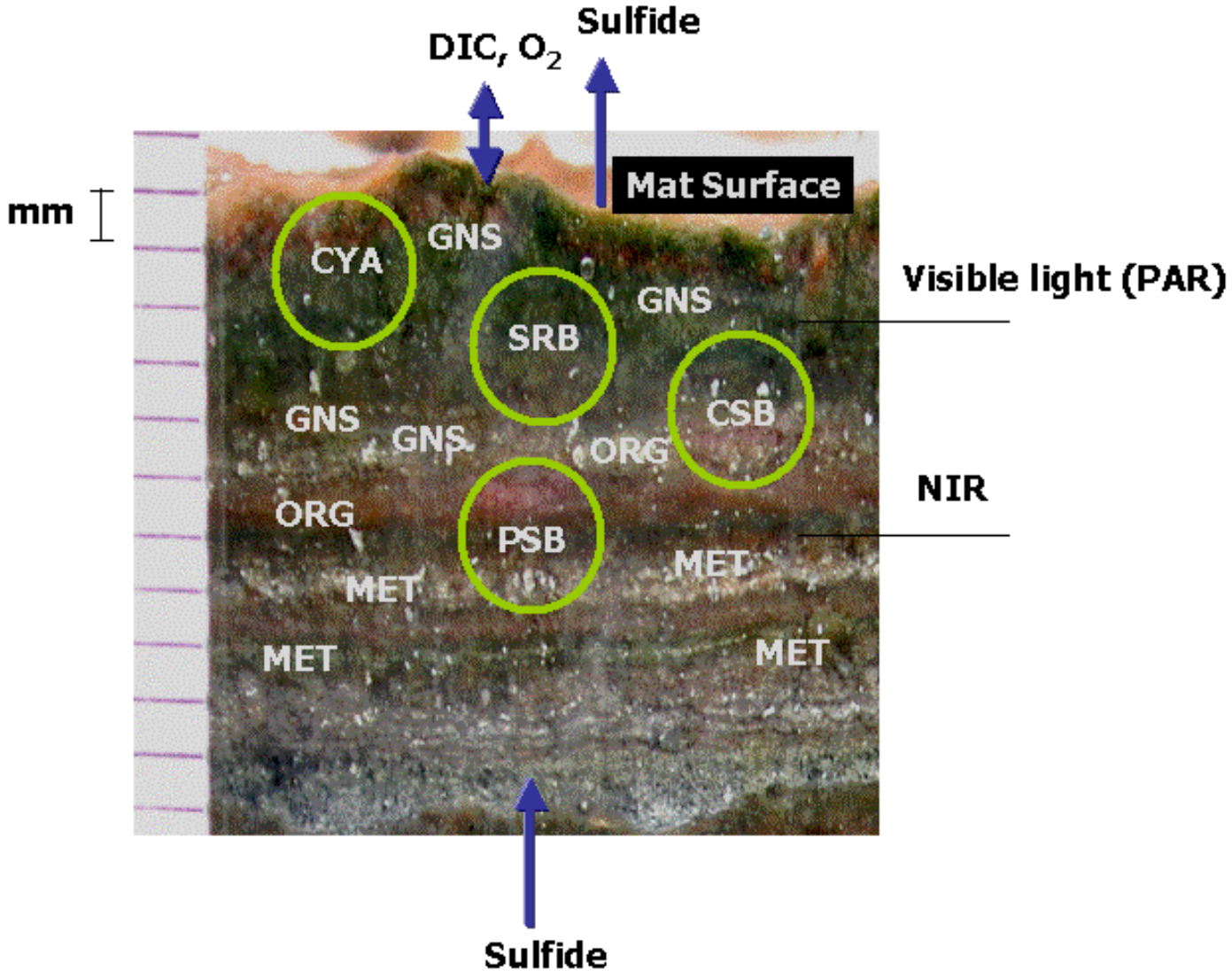


Time (Millions of Years Ago)

Oxygenic photosynthesis ~ 0.5 billion years before the GOE is consistent with some, but not all textural and geochemical proxies

(Fournier et al., *Proc Roy Soc B*, 2021)

Spatial Organization of Metabolisms and Minerals in Microbial Mats



http://geo.arc.nasa.gov/sge/casa/microbial/microbial.html

Silicate Weathering Provides Cations and Inorganic Carbon to Natural Waters

$K_2O{\cdot}Al_2O_3{\cdot}6SiO_2$ (s) + $2CO_2$ (aq) + 2.4 H_2O=

$2K^+ + 2HCO_3^- + Al_2O_3{\cdot}2SiO_2$ (s) + $2.6SiO_2$(s) + $1.4H_2SiO_3$ (aq)

Igneous rock + CO_2 + water = cations + clays + silicic acid + silica dioxide

Weathering of silicates removes CO_2 from the surface

Dissolved Inorganic Carbon Species

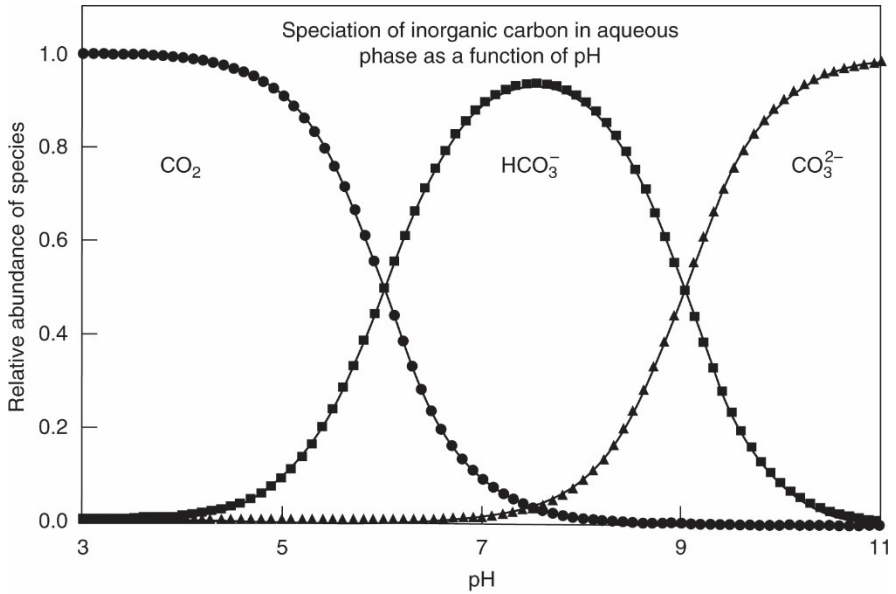


Figure 2.1 The relative distribution of the three major species of dissolved inorganic carbon in water as a function of pH. Note that at pH of seawater (~8.1), approximately 95% of the inorganic carbon is in the form of bicarbonate anion.

Carbonate Precipitation and Alkalinity

Alkalinity: net concentration of strong base in excess of strong acid

$Alk = -[H^+] + [OH^-] + [HCO_3^-] + 2[CO_3^{2-}] = [STRONG\ BASE]_T$

Carbonate precipitation or dissolution determined by the solubility constant

$$K_s = [Ca^{2+}][CO_3^{2-}] \text{ at equilibrium}$$

If $[Ca^{2+}][CO_3^{2-}] > K_s$, carbonate minerals can precipitate

Evaporate Sequence and Mineral Solubility in Salterns

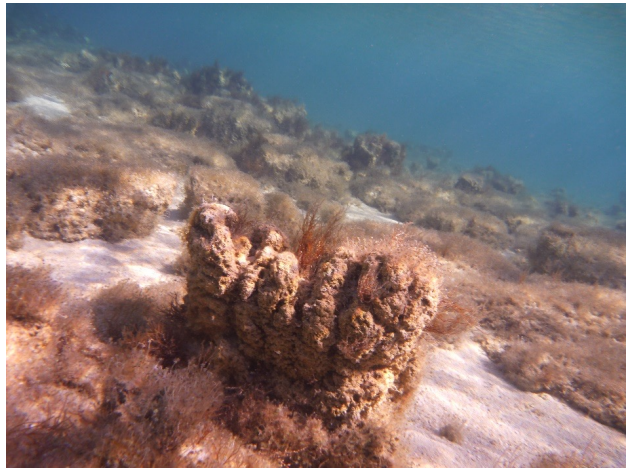
Halite (NaCl) : $Ks=10^{1.5}$

Calcite: $Ks=10^{-8.35}$

Gypsum: $Ks=10^{-4.6}$

Water flows in a cascade from the shallow ponds where calcite/dolomite precipitate, to ponds where gypsum precipitates, to ponds where NaCl precipitates (now devoid of other minerals).

Modern Stromatolites From Western Australia – Evaporative Basin



https://www.youtube.com/watch?v=uzwvjOSS2Pc

Oxygenic Photosynthesis

$2HCO_3^- + Ca^{2+} \rightarrow CH_2O + O_2 + CaCO_3$

*psa*ABCDEFL *psb*ABCDEFOTUV *pet*ABCD *atp*ABCDEFGH *pet*CEH

→ Fermentation; N_2 Fixation

Aerobic Heterotrophy

$CH_2O + CaCO_3 + O_2 \rightarrow 2HCO_3^- + Ca^{2+}$

adhE LDH

→ Fermentation; Bchl Synthesis; Glycogen Degradation

Anoxygenic Photosynthesis

$3HCO_3^- + Ca^{2+} + HS^- \rightarrow 2CH_2O + CaCO_3 + SO_4^{2}$

*puf*BLM *puf*H *bch*XYZ

→ Fermentation; Denitrification

Aerobic Sulfide Oxidation

$HS^- + 2O_2 + CaCO_3 \rightarrow SO_4^{2-} + Ca^{2+} + HCO_3^-$

sox

→ Fermentation; Denitrification

Sulfate Reduction

$2CH_2O + SO_4^{2-} + OH^- + Ca^{2+} \rightarrow CaCO_3 + CO_2 + 2H_2O + HS^-$

*apr*AB *dsr*AB *sat met*3 *cys*CDHIJNQ PAPSS *sir*

→ Sulfate Reduction

Methanogenesis

$2HCO_3^- + 4H_2 + Ca^{2+} \rightarrow CaCO_3 + CH_4 + 2H_2O$

*mcr*A *hdr*ABC2 *mvh*ADG *vhu*ADG *vhc*ADG *fwd*ABF *fmd*ABF *mtr*AH *mtt*B

→ Methanogeneis

Fermentation

$3CH_2O + CaCO_3 + H_2O \rightarrow 2HCO_3^- + Ca^{2+} + C_2H_6O$

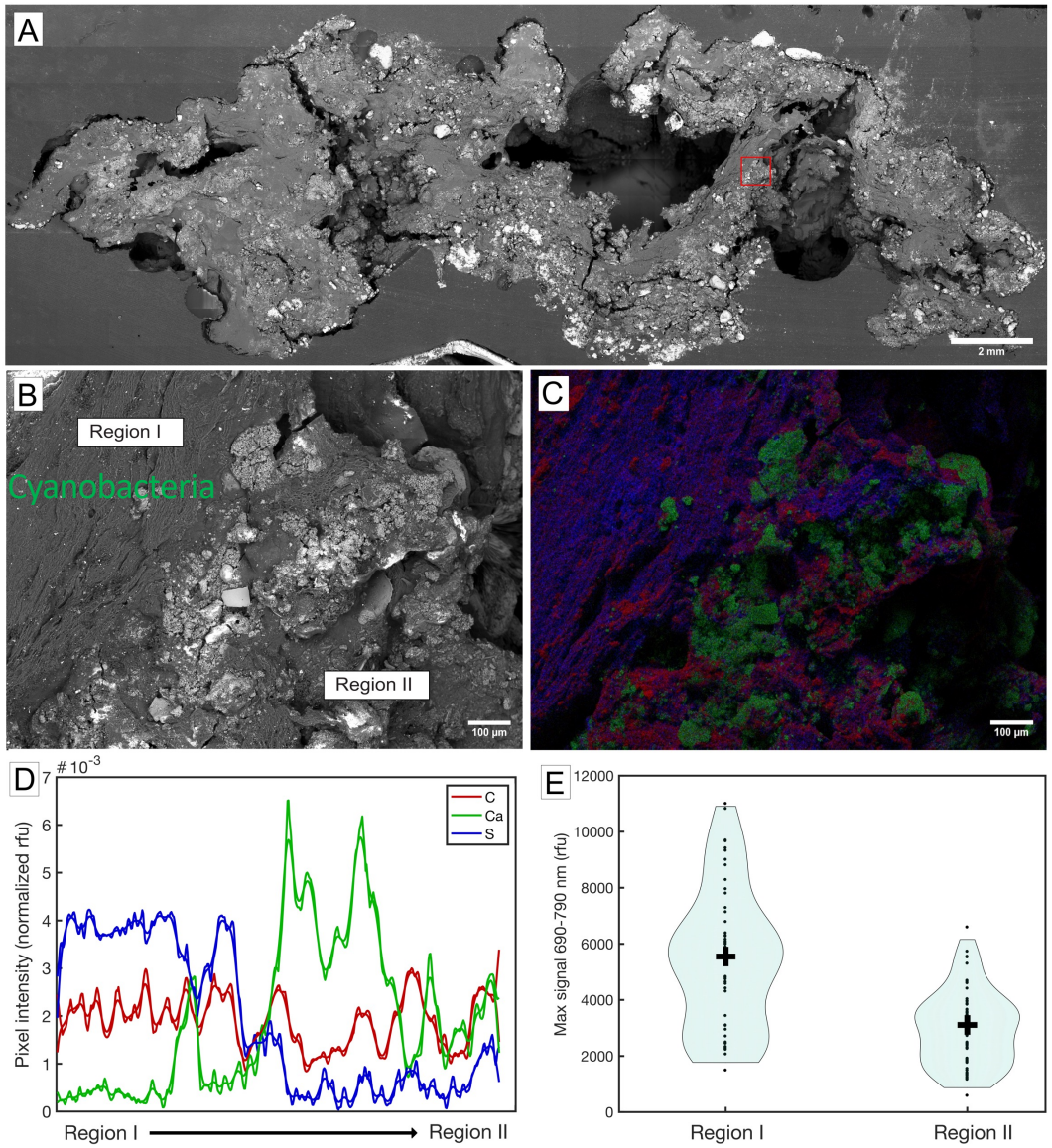
HoxEFU adhE LDH

→ Fermentation

Promoting Precipitation **Promoting Dissolution**

(Cutts et al., 2022)

EPS Composition and Lithification in Modern Stromatolites

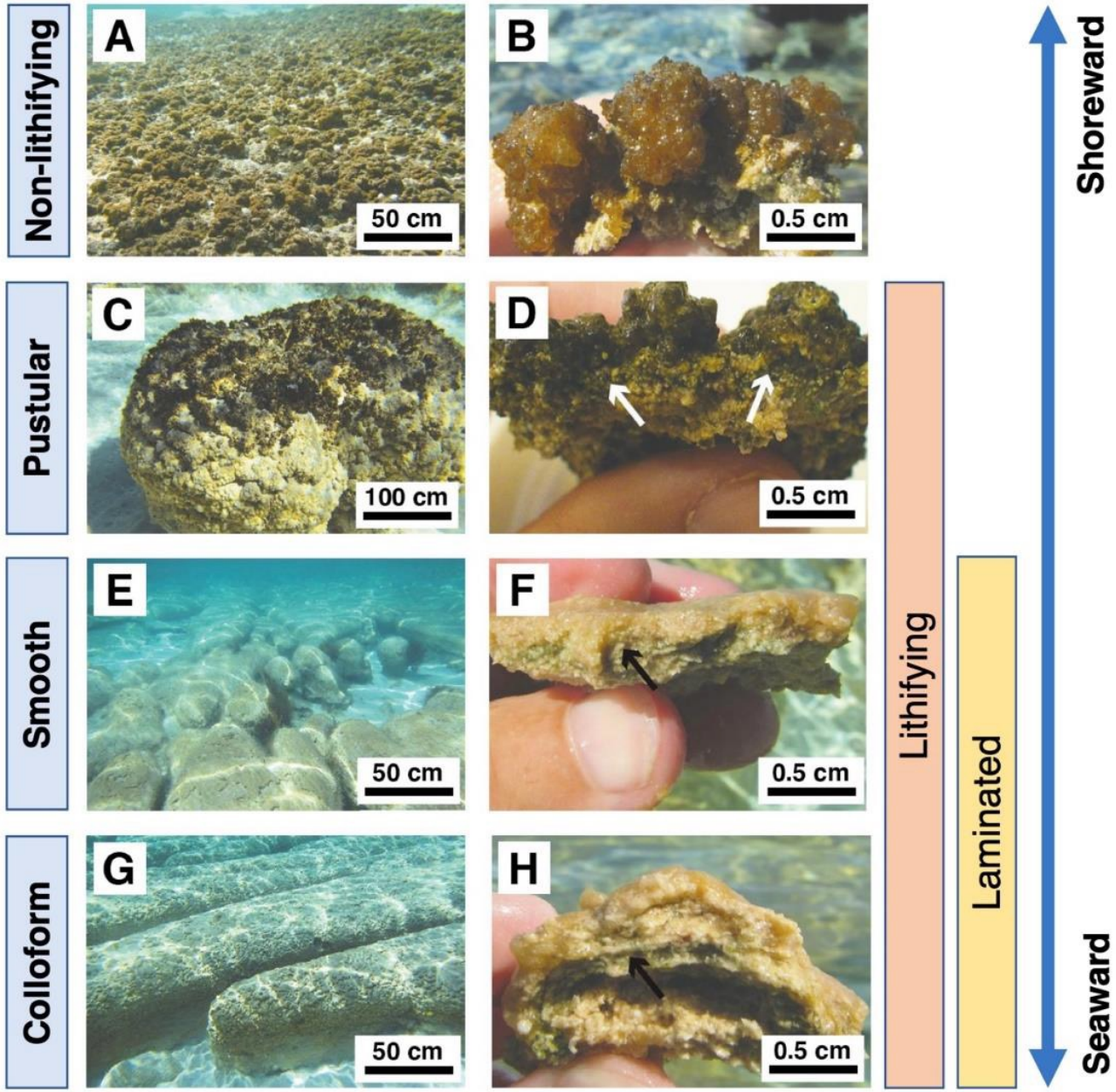


Sulfated polysaccharides

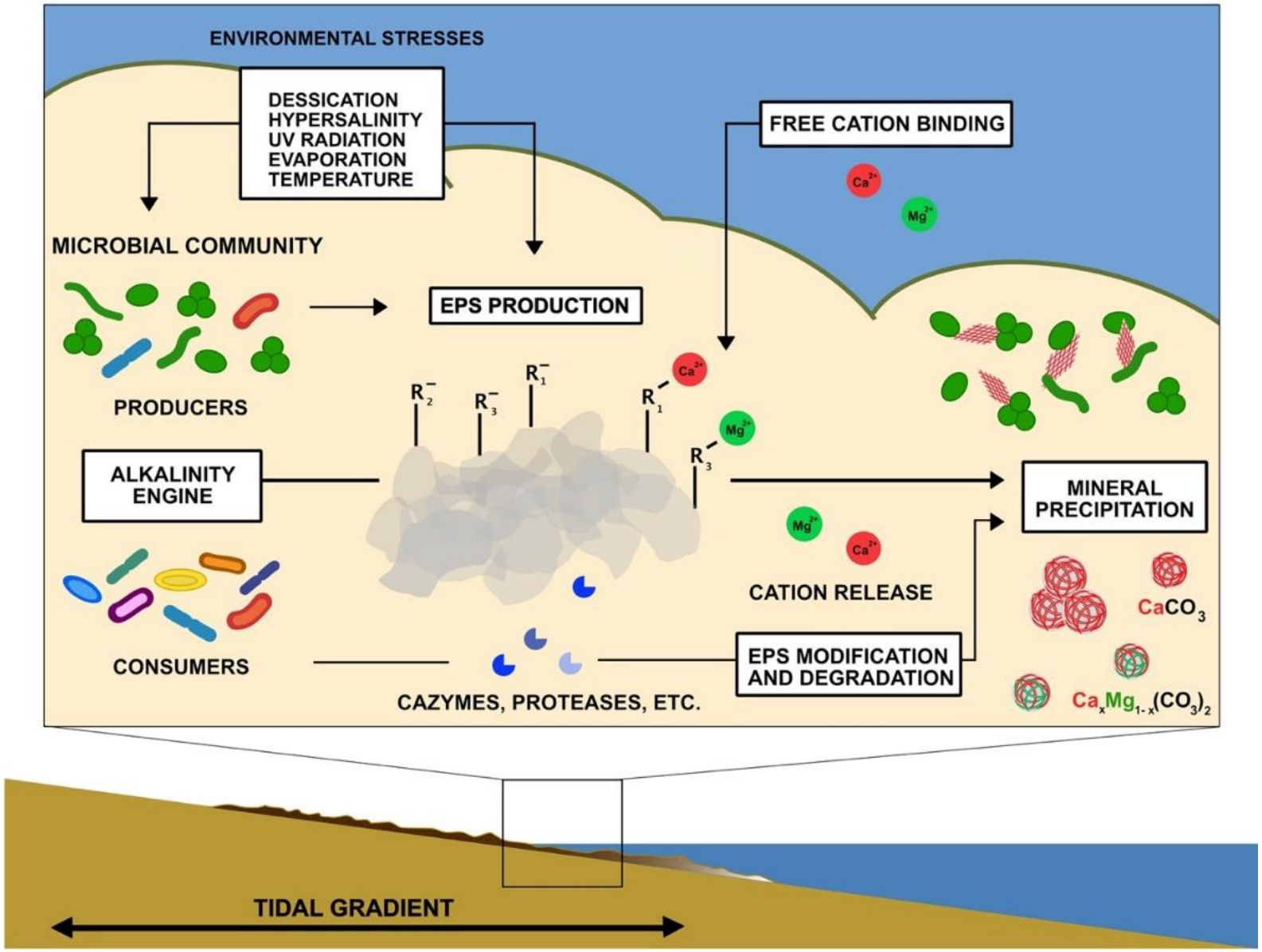
Carbonate minerals

Other polysaccharides

(Skoog et al., 2022)



(Cutts et al., 2022)



(Cutts et al., 2022)