

# Some background MSE 493

Prof. Tiffany Abitbol 2024



How was it?



### Dual carbon sequestration with photosynthetic living materials

Dalia Dranseike<sup>1,#</sup>, Yifan Cui<sup>1,#</sup>, Andrea S. Ling<sup>2</sup>, Felix Donat<sup>3</sup>, Stéphane Bernhard<sup>1</sup>, Margherita Bernero<sup>4</sup>, Akhil Areeckal<sup>1</sup>, Xiao-Hua Qin<sup>4</sup>, John S. Oakey<sup>5</sup>, Benjamin Dillenburger<sup>2</sup>, André R. Studart<sup>6</sup>, and Mark W. Tibbitt<sup>1,\*</sup>

<sup>&</sup>lt;sup>1</sup> Macromolecular Engineering Laboratory, Department of Mechanical and Process Engineering, ETH Zurich, Zurich, CH.

<sup>&</sup>lt;sup>2</sup> Digital Building Technologies, Department of Architecture, ETH Zurich, Zurich, CH.

<sup>&</sup>lt;sup>3</sup> Laboratory of Energy Science and Engineering, Department of Mechanical and Process Engineering, ETH Zurich, Zurich, CH.

<sup>&</sup>lt;sup>4</sup> Institute for Biomechanics, Department of Health Sciences and Technology, ETH Zurich, Zurich, CH.

<sup>&</sup>lt;sup>5</sup> Department of Chemical and Biomedical Engineering, University of Wyoming, Laramie, Wyoming, US.

<sup>&</sup>lt;sup>6</sup> Complex Materials, Department of Materials, ETH Zurich, Zurich, CH.

<sup>#</sup>equally contributing authors

<sup>\*</sup>corresponding author: mtibbitt@ethz.ch



#### **Abstract**

Natural ecosystems offer efficient pathways for carbon sequestration, serving as a resilient approach to remove CO<sub>2</sub> from the atmosphere with minimal environmental impact. However, the control of living systems outside of their native environments is often challenging. Here, we engineered a photosynthetic living material for dual CO<sub>2</sub> sequestration by immobilizing photosynthetic microorganisms within a printable polymeric network. The carbon concentrating mechanism of the cyanobacteria enabled accumulation of CO<sub>2</sub> within the cell, resulting in biomass production. Additionally, the metabolic production of OH<sup>-</sup> ions in the surrounding medium created an environment for the formation of insoluble carbonates via microbially-induced calcium carbonate precipitation (MICP). Digital design and fabrication of the living material ensured sufficient access to light and nutrient transport of the encapsulated cyanobacteria, which were essential for long-term viability (more than one year) as well as efficient photosynthesis and carbon sequestration. The photosynthetic living materials sequestered approximately 2.5 mg of CO<sub>2</sub> per gram of hydrogel material over 30 days via dual carbon sequestration, with  $2.2 \pm 0.9$  mg stored as insoluble carbonates. Over an extended incubation period of 400 days, the living materials sequestered 26 ± 7 mg of CO<sub>2</sub> per gram of hydrogel material in the form of stable minerals. These findings highlight the potential of photosynthetic living materials for scalable carbon sequestration, carbon-neutral infrastructure, and green building materials. The simplicity of maintenance, coupled with its scalability nature, suggests broad applications of photosynthetic living materials as a complementary strategy to mitigate CO<sub>2</sub> emissions.

### Keywords:

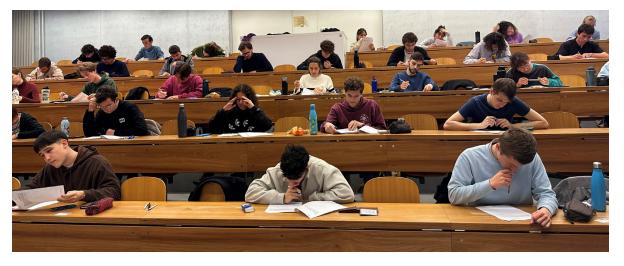
- 1. Carbon
- 2. Carbon sequestration
- 3. Photosynthesis
- 4. MICP
- 5. Cyanobacteria
- 6. Hydrogel last few weeks
- 7. 3D printing last week
- 8. Photosynthetic living materials

Keywords: living materials, CO<sub>2</sub> sequestration, 3D printing

## Flashback to simpler times: MSE 341 Sustainability and Materials



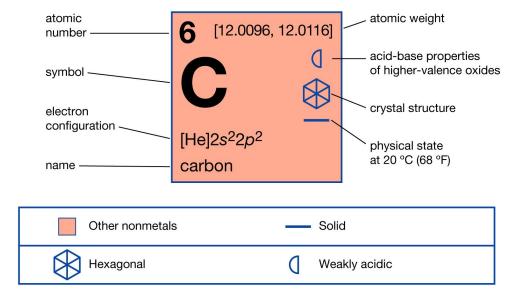






## **EPFL** Carbon

#### Carbon



© Encyclopædia Britannica, Inc.

• 18% of human body (second element after oxygen)

### **Energy currency**

- Energy released when bonds are broken to drive cellular processes
- Fuel food, wood, gas, oil, etc.,

### **Materials currency**

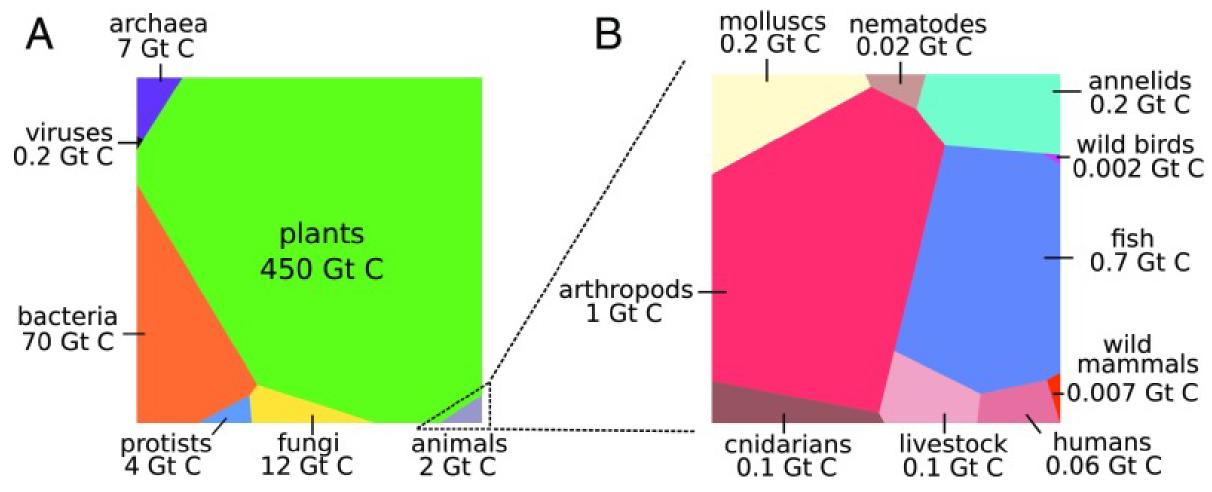
- Carbon is consumed and restructured to produce new biomass
- Plastic, diamond, graphite, steel, etc..

### **Temperature regulation**

 Fast (year-scale) and slow (million-year scale) carbon cycles

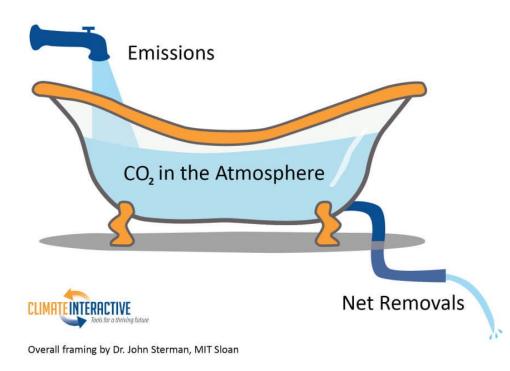


## **Total global live biomass – 550 billion tonnes carbon**

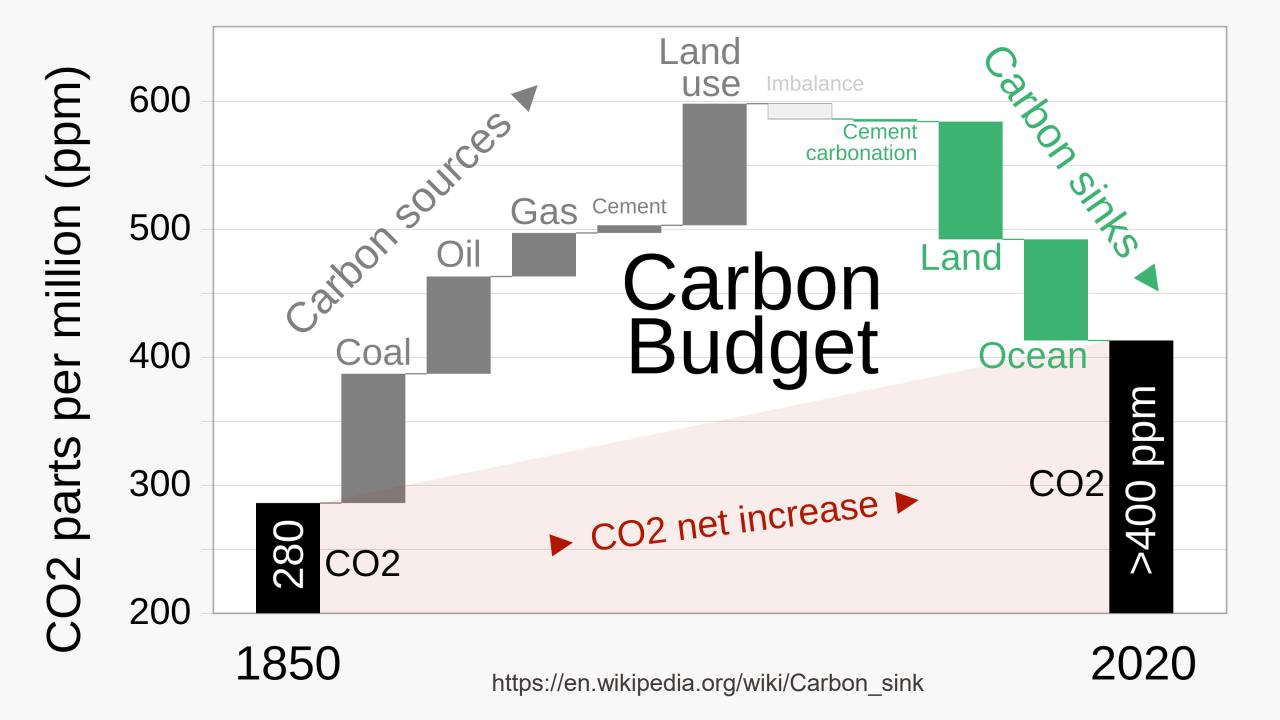


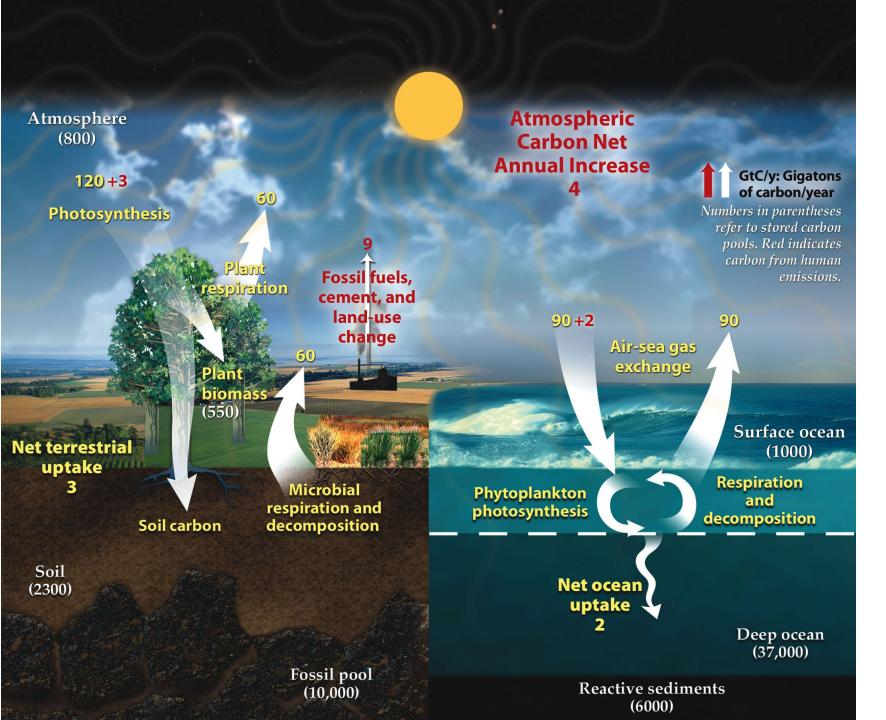
### **Sinks and Pools**

- A pool is the places that carbon can be stored: atmosphere, oceans, soil, etc.,
- A sink is a type of pool that takes in more atmospheric carbon than it releases
- Most important sinks globally: vegetation, ocean



**Climate Bathtub Simulation** 





Global pools of carbon (white): oceans (the largest reservoir), geological reserves of fossil fuels, the terrestrial surface (plants and soil, mainly), and the atmosphere.

### Fast carbon cycle:

- Yellow (natural fluxes)
- Red (anthropogenic)
- White (stored carbon)

Slow carbon cycle (not shown)

Volcanic/tectonic activities

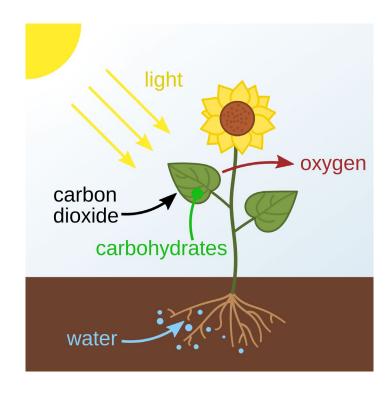
Global warming accelerates soil respiration Nature 2023

Carbon cycle

## **Energy production**

- In most ecosystems, the sun is the source of all energy
- Autotrophs fix CO<sub>2</sub> from the atmosphere into organic compounds like sugars, lipids, and proteins
- Photoautotrophs, plants and microorganisms (algae, cyanobacteria), use photosynthesis to produce biomass
- They absorb specific wavelengths of sunlight using the pigment chlorophyll (or other) converting sunlight to chemical energy (energy stored in bonds)
- Heterotrophs (like humans) don't do photosynthesis, instead consume these sugars, lipids, and proteins and use the stored energy to power their activities
- Fossil fuels are derived from organic materials, converted by heat and pressure to oil, coal, or natural gas over geologic time "fossilized sunlight" – slow cycle

### Carbon sequestration?



Photosynthesis:  $6CO_2 + 6H_2O + light energy \rightarrow C_6H_{12}O_6 (glucose) + 6O_2$ 

Photosynthesis

Wavelength [nm]



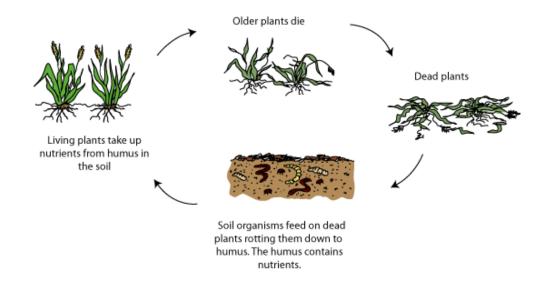


- Comes from Greek for green (chloros) leaf (phyllon)
- Chlorophyll a absorbs violet and orange
- Chlorophyll b absorb blue and yellow
- (cyanobacteria also have phycobiliproteins; phycocyanin and allophycocyanin)

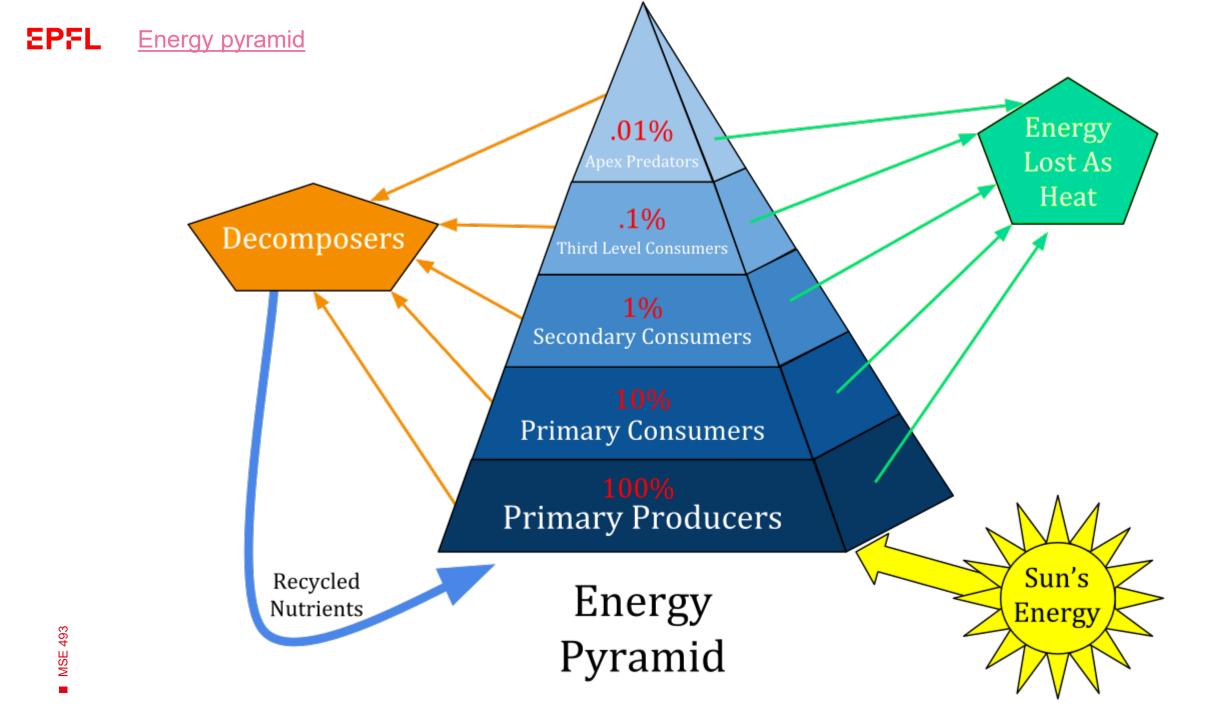


## **Energy consumption**

- The sugars, lipids, and proteins generated by plants and microbes store energy from the sun in carbon-hydrogen (C-H) bonds (chemical energy)
- These are broken down in cells to release energy via respiration, and we also break them down from our fuel tanks to release energy via combustion
- Although respiration and combustion are very different, they ultimately produce the same result, which is to use oxygen to convert organic compounds containing C-H bonds back into CO<sub>2</sub>
- Some organisms use the energy produced by plants directly, some eat organisms that ate plants, some eat organisms that ate organisms that ate plants, and so on; some organisms use a mixture of carbon sources and some use waste products, but ultimately food webs lead back to the energy produced by plants and microbes (primary producers)



Respiration:  $C_6H_{12}O6 + 6O_2 \rightarrow 6CO_2 + 6H_2O + chemical$  energy (ATP)





## **Energy balance**

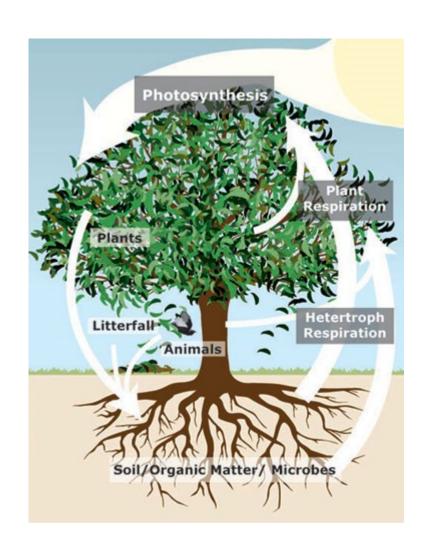
### Photosynthesis:

 $6CO_2 + 6H_2O + light energy \rightarrow C_6H_{12}O_6 (glucose) + 6O_2$ 

### Respiration:

 $C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O + chemical energy$ 

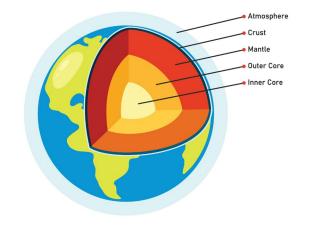
- Fast cycle operates in biosphere
- Equations tend to balance over time
- CO<sub>2</sub> fixed by photosynthesis is eventually returned to the atmosphere
- Oxygen and water also tend to balance
- Net effect of photosynthesis is light energy converted to chemical energy (sunlight that fuels the entire ecosystem)
- Why does burning fossil fuels imbalance the carbon cycle? Hint fast/slow cycles



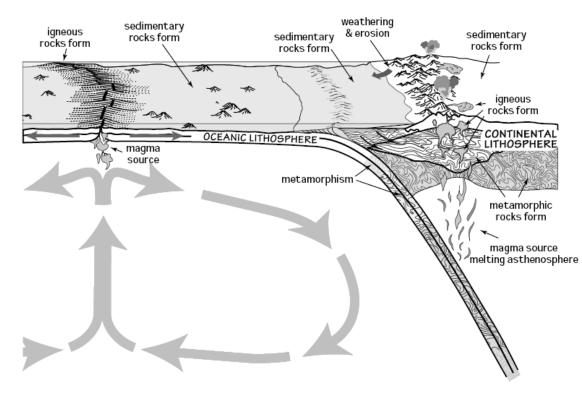


### Slow carbon cycle:

- Moves carbon through crust, between rocks, soil, ocean, and atmosphere (10-100 million tonnes of carbon per year)
- Carbon in the ocean precipitates to the ocean floor where it can form sedimentary rock and be subducted into the Earth's mantle
- Mountain building processes result in the return of this geologic carbon to the Earth's surface
- Weathering of rocks returns carbon to the atmosphere and ocean
- Exchange between the ocean and atmosphere can take centuries
- Weathering of rocks can take millions of years



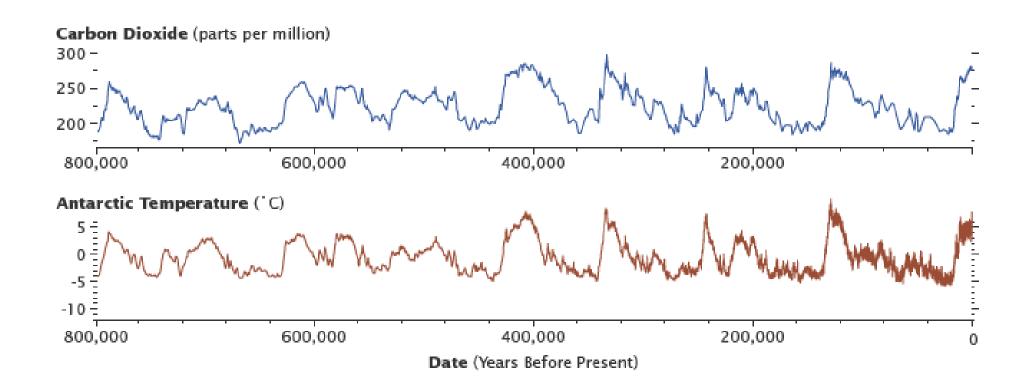
## The Rock Cycle



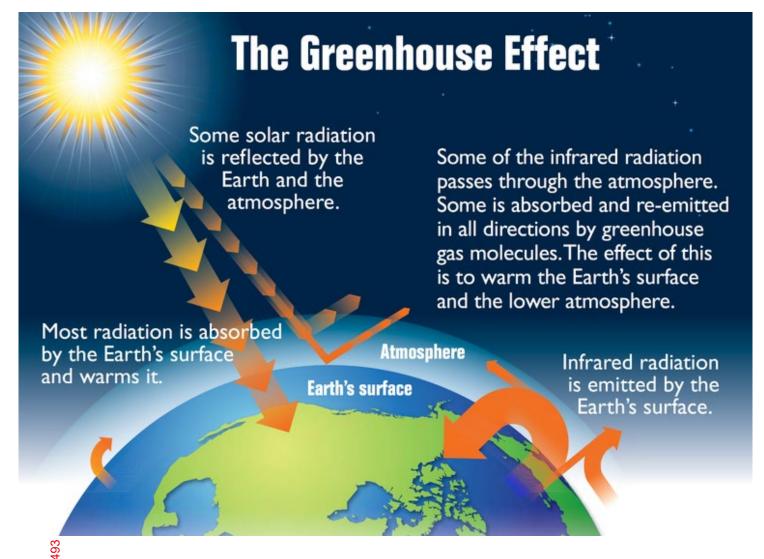


## Natural variations in the carbon cycle

 Left-unperturbed, the planet maintains a relatively stable concentration of CO<sub>2</sub> in the atmosphere, with a close correspondence to temperature



## **Greenhouse effect – it's not global warming!**

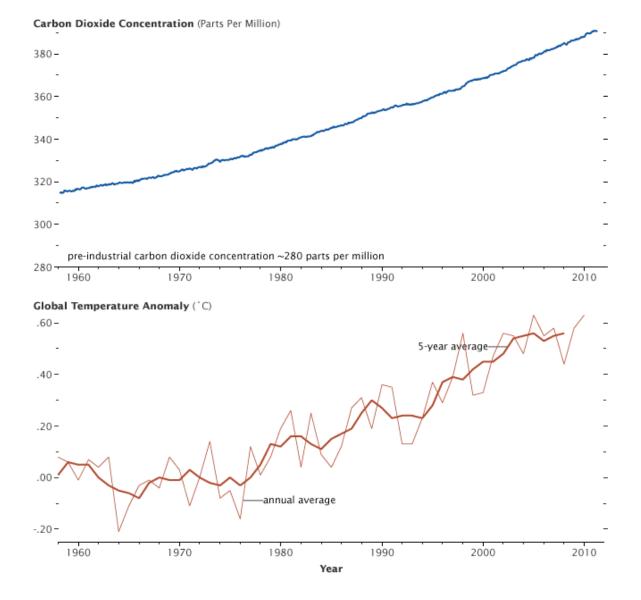


- "Blanket" of gases around the planet
- Naturally part of makeup of the atmosphere
- Sunlight absorbed by earth and re-emitted as infrared (heat)
- Some infrared passes through the atmosphere, some absorbed and re-emitted by greenhouse gases (GHGs) in all directions to heat the Earth's surface and lower atmosphere
- "Goldilocks planet" not too hot or too cold
- Helps maintain temperature at 15 °C (avg)



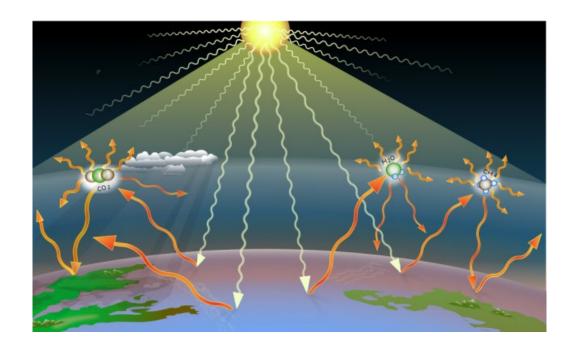
https://climate.nasa.gov/fag/19/what-is-the-greenhouse-effect/ https://energyeducation.ca/encyclopedia/Greenhouse effect

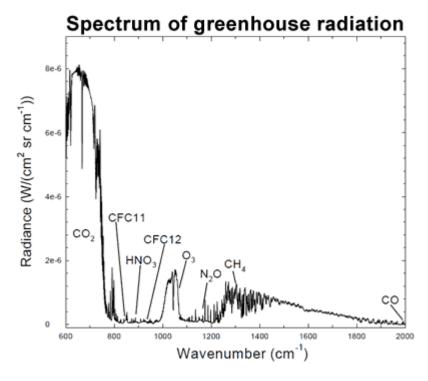
## What if we perturb the cycle?



- Slow cycle takes ca. 100 million years, whereas the fast cycle takes ca. 10-100 years (living thing lifespan)
- By burning fossil fuels, we shift carbon from the slow cycle into the fast cycle (carbon from the Earth's crust is extracted and burned for energy)
- Corresponding increase in global temperature anomaly

## **Global warming**





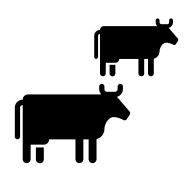
- Earth absorbs sunlight and reradiates it as infrared (heat)
- GHGs absorb specific infrared wavelengths
- If unimpeded, infrared travels through the atmosphere and back into space
- Too high a concentration of GHGs (like CO<sub>2</sub>) is a problem, as these gases absorb infrared light, re-emit it in all directions, leading to warming beyond the greenhouse effect – global warming



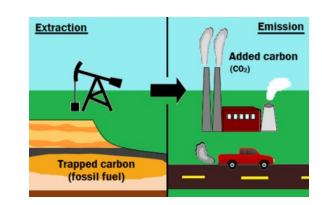
## Greenhouse gases (GHGs)

### Gases that trap heat in the atmosphere:

- Carbon dioxide (CO<sub>2</sub>) burning fossil fuels, solid waste, trees, biological materials, chemical reactions (cement manufacture)
- Methane (CH<sub>4</sub>) production/transport of coal, natural gas, oil, agriculture/livestock emissions, decay of organic waste in municipal solid waste landfills



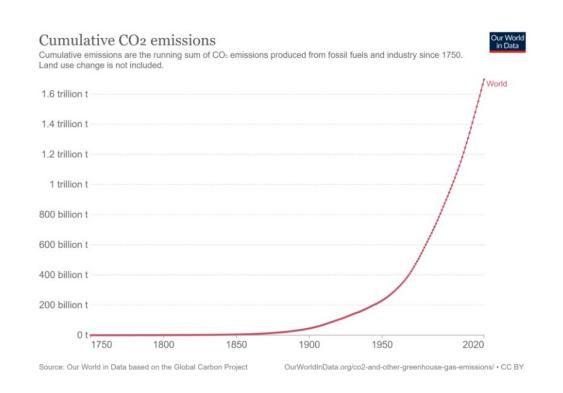
- Nitrous oxide (N<sub>2</sub>O) agriculture, fuel combustion, wastewater management, and industrial processes
- Fluorinated gases various household, commercial, industrial uses, emitted at lower amounts but have a high global warming potential (GWP), for a given amount of mass trap way more heat than CO<sub>2</sub>

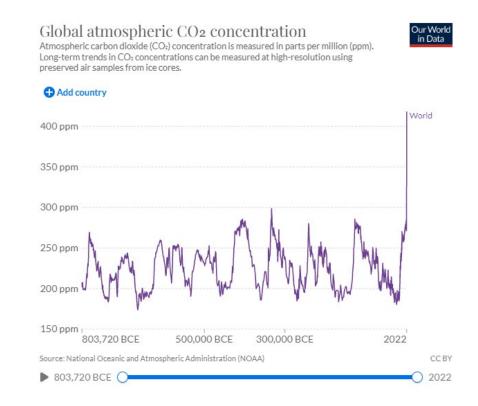




## **Anthropogenic activities related to carbon emissions**

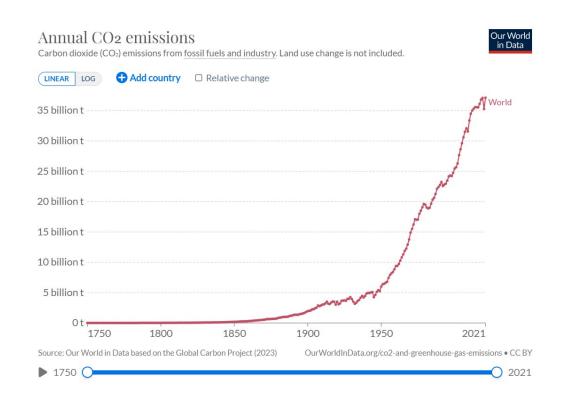
- CO<sub>2</sub> emissions associated with human activity
- Most of the increase occurring after 1950

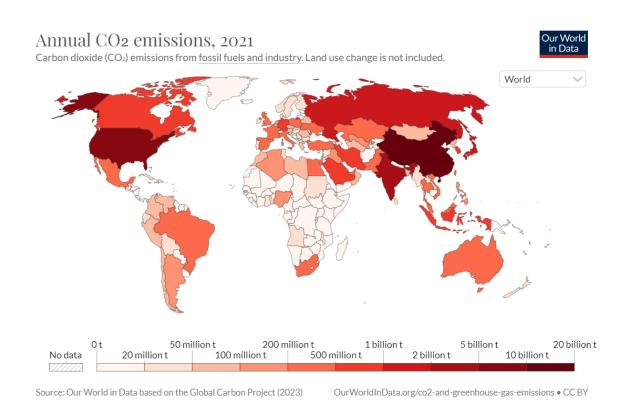




## **Carbon emissions** (fossil fuels + industry)

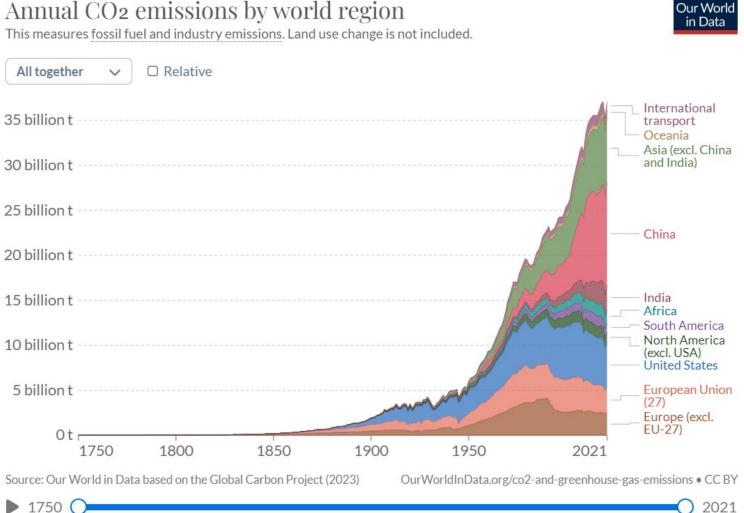
### Global CO2 emissions





- In 1950 6 billion tonnes global CO<sub>2</sub> emissions
- In 1990 almost 4-fold increase to 22 billion tonnes
- Current more than 34 billion tonnes/year

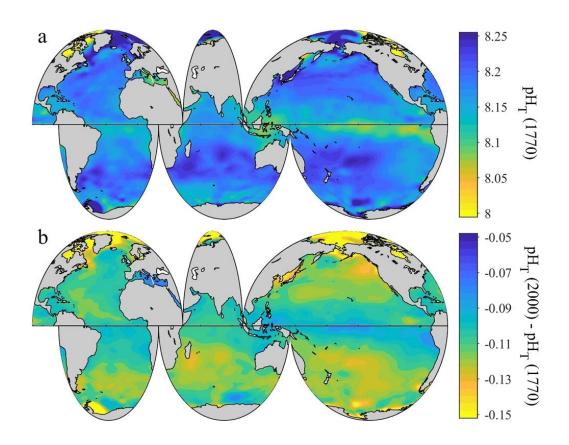
## **Carbon emissions**





- Well into 20<sup>th</sup> century, emissions dominated by Europe and US – e.g., 90% of emissions in 1900, and >85% of annual emissions even by 1950
- Scenario changed after 1950 with significant rise in emissions in the rest of the world, most notably in China
- Europe and US now account for less than 1/3 of global emissions

## Ocean acidification



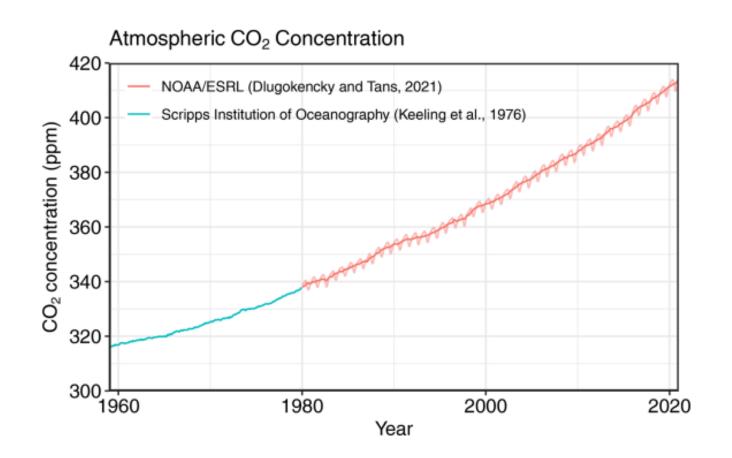
Jiang, LQ., Carter, B.R., Feely, R.A. *et al.* Surface ocean pH and buffer capacity: past, present and future. *Sci Rep* **9**, 18624 (2019). https://doi.org/10.1038/s41598-019-55039-4

### Dynamic equilibrium:

- $H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$
- $HCO_3^- \rightleftharpoons 2H^+ + CO_3^{2-}$
- Typically this buffering system keeps ocean pH relatively stable at around 8
- Too much CO<sub>2</sub>, buffer capacity is reduced, and net effect is acidification
- Interferes with shell formation
- Colder waters are more vulnerable to acidification due to their ability to hold more dissolved gases

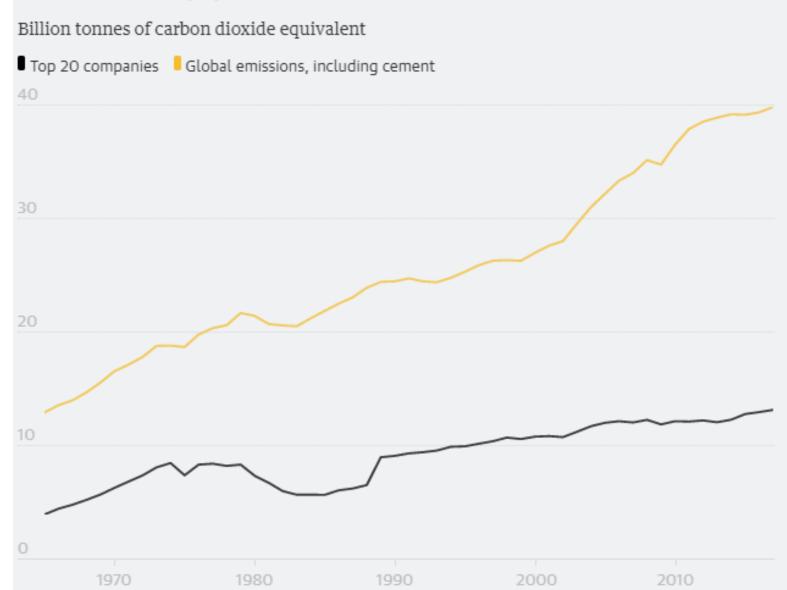
## Global carbon breakdown

 Emissions up 49% from pre-industrial levels to 421 ppm in 2022 from 277 ppm in 1750



Global carbon budget

## The top 20 companies have contributed to 35% of all carbon dioxide and methane since 1965



Guardian graphic | Source: Richard Heede, Climate Accountability Institute

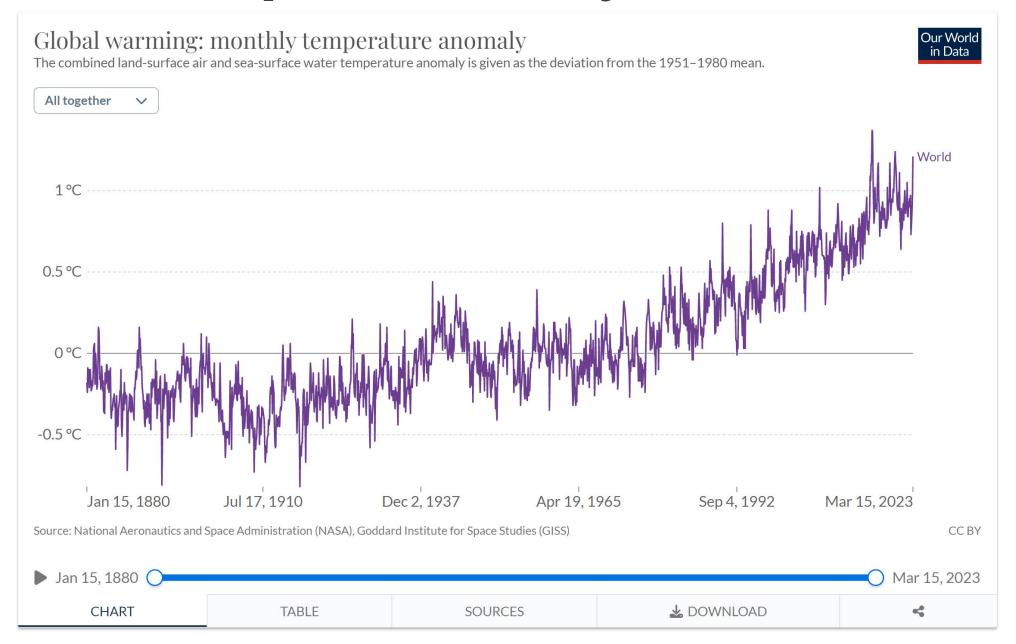
# Top 20 CO<sub>2</sub> emitting companies

"The great tragedy of the climate crisis is that seven and a half billion people must pay the price - in the form of a degraded planet – so that a couple of dozen polluting interests can continue to make record profits. It is a great moral failing of our political system that we have allowed this to happen."

The Guardian article\_2019

period 1965 to 2017 only

## **Global temperature anomaly**





## **Anthropogenic carbon**

Where does it come from?



**89%** 34.8 GtCO<sub>2</sub>/yr



- Mainly from burning fossil fuels
- Small part from new cement



**11%** 4.1 GtCO<sub>2</sub>/yr

Emissions from land use change

(mostly deforestation)

## **Anthropogenic carbon**



48% 18.6 GtCO<sub>2</sub>/yr Atmosphere

Where does it go?



29% 11.2 GtCO<sub>2</sub>/yr

### Vegetegation & Soils

(terrestrial biosphere)

From 2011-2020: about 55% of global emissions absorbed by terrestrial biosphere and oceans

The remainder goes to the atmosphere!



26% 10.2 GtCO<sub>2</sub>/yr

### Oceans

(terrestrial biosphere)

Global carbon budget Global Carbon Project

CO<sub>2</sub> to transport and storage

Flue gas from burning fossil fuels: 70% N<sub>2</sub>, 15% CO<sub>2</sub>,

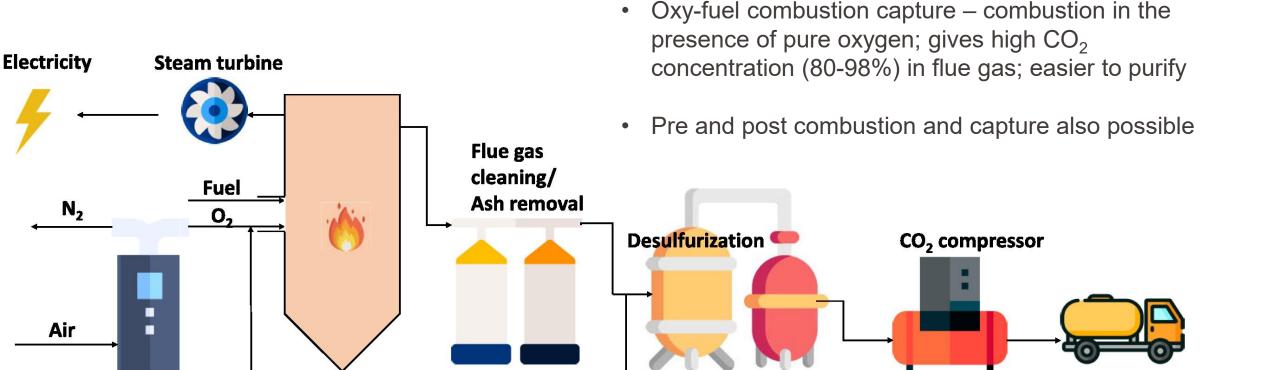
lesser amounts H<sub>2</sub>O, NO<sub>x</sub>, CO, SO<sub>x</sub>

Cooler and

condenser

### **EPFL**

## **Limiting CO<sub>2</sub> emissions**



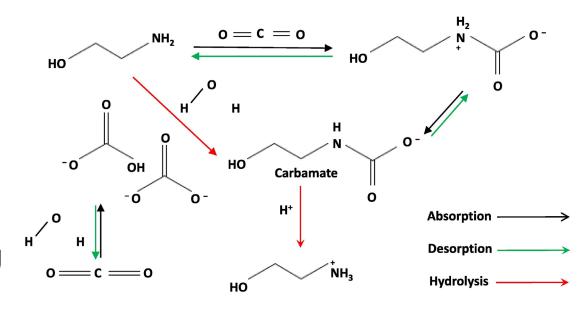
Air separation unit

**Boiler** 

**Recycled flue gas** 

## Conventional CO<sub>2</sub> capture - absorption

- Gas mixture containing CO<sub>2</sub> is reacted with a solvent that can dissolve gaseous CO<sub>2</sub> into a liquid phase
- Depending on solvent, absorption can be physical or chemical
- In chemical absorption, solvents, like MEA (monoethanolamine) or other amine-based alkali solvents, form strong bonds with CO<sub>2</sub> under atmospheric conditions
- First method that has been implemented on an industrial-scale for postcombustion carbon capture



Other methods: Adsorption Membranes



## What can we do with CO<sub>2</sub> after it is captured? Storage & utilization

### Storage:

- 1. Geological storage (underground, depleted oil/gas reservoirs)
- Ocean storage (deep water/sea floor)
- 3. Mineral carbonation (convert CO<sub>2</sub> to insoluble carbonates)

### **Utilization:**

- Enhanced oil recovery (EOR) inject CO<sub>2</sub> into oil fields to enhance oil recovery, CO<sub>2</sub> remains underground after oil extraction
- 2. Industrial uses manufacture of fuels, chemicals, materials
- 3. Agriculture enhancing plant growth in greenhouses
- 4. Food and beverage carbonation, preservation
- 5. Biofuel feeding to bacteria or algae to produce biofuel



## **Carbon capture and storage (CCS)**

- CCS dates back to the 1970s idea of collecting, pipeline transporting, and storing CO<sub>2</sub> into deep ocean reservoirs or cavities of natural gas and oil – preventing its emission to the atmosphere (2018 Nobel Prize in Economics)
- Worry risk of ocean acidification caused by leaks
- From article: only 19 active CCS facilities, with an annual storage capacity pf 40 million tons, equivalent to about 0.1% total annual CO<sub>2</sub> emissions

# How many Gt of CO<sub>2</sub> do we need to remove from the atmosphere?

1 Gt = 1 billion metric tonnes Ppm = parts per million Mass of the atmosphere =  $5.1 \times 10^{18}$  kg MW of air is 29 g/mol (mix of gases, 78% nitrogen) MW of  $CO_2$  = 44 g/mol

- Let's say we would like to remove 100 ppm of CO<sub>2</sub> from the atmosphere to bring us down to 300 ppm
- Mass of 100 ppm CO<sub>2</sub> in atmosphere = 100/1000000\* 5.1 ×10<sup>18</sup> kg\* 44/29 = 7.7 ×10<sup>14</sup> kg = 770 Gt
- Geological storage capacity is estimated at 675-900 Gt for depleted oil/gas fields & 1000-10000 Gt for deep saline formations
- Easy peasy? (Capturing CO<sub>2</sub> from air is not straightforward and highly energy intensive!)

## Carbon capture, utilization, and storage (CCUS)

- Enhanced oil recovery (EOR)
- Enhanced gas recovery (EGR)
- Enhanced coalbed recovery (ECBR)
- Enhanced water recovery
- Is continuing fuel extraction a good long term solution?

### **CCU and CCUS**

 CCU and CCUS are viewed as "short-term partial solutions to reduce atmospheric CO<sub>2</sub> concentrations?"

### Why?

- Address symptoms (high CO<sub>2</sub> levels) but not root cause (emissions)
- Buy time until better solutions can be developed and implemented
- 85-95% capture rates
- Target point sources
- Enormous infrastructure would need to be put in place
- High cost and energy requirements
- Limits to the amount of CO<sub>2</sub> that can be safely stored underground



# Mineral carbonation as a mimic for natural weathering

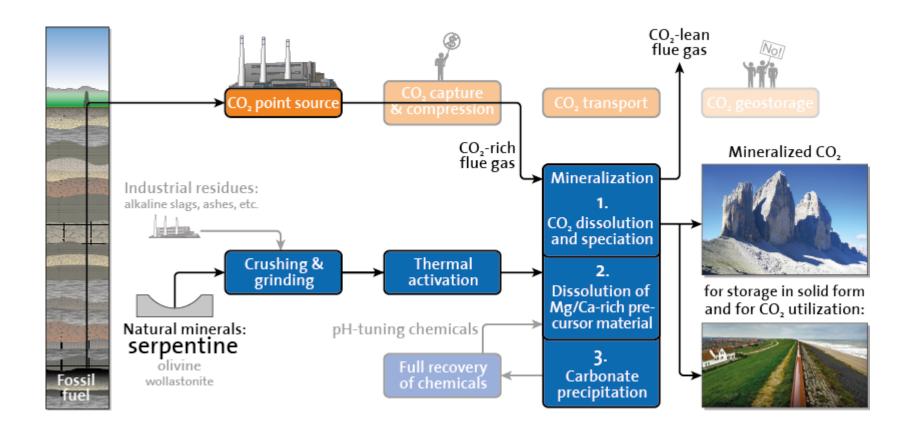
### Natural weathering:

- Rocks rich in calcium and magnesium silicates react with CO<sub>2</sub> over long period in a process called chemical weathering
- CO<sub>2</sub> dissolves in rain water, forming carbonic acid (H<sub>2</sub>CO<sub>3</sub>), which reacts with the silicate minerals, producing bicarbonate (HCO<sub>3</sub>-) and metal ions. These ions can precipitate as carbonate minerals (e.g., limestone).

### **Engineered weathering:**

 CO<sub>2</sub> is captured from industrial sources or air, mixed with water to form carbonic acid solution & exposed to finely ground silicates, producing bicarbonate and metal ions, which can be precipitated into carbonate minerals

## **Mineralization**

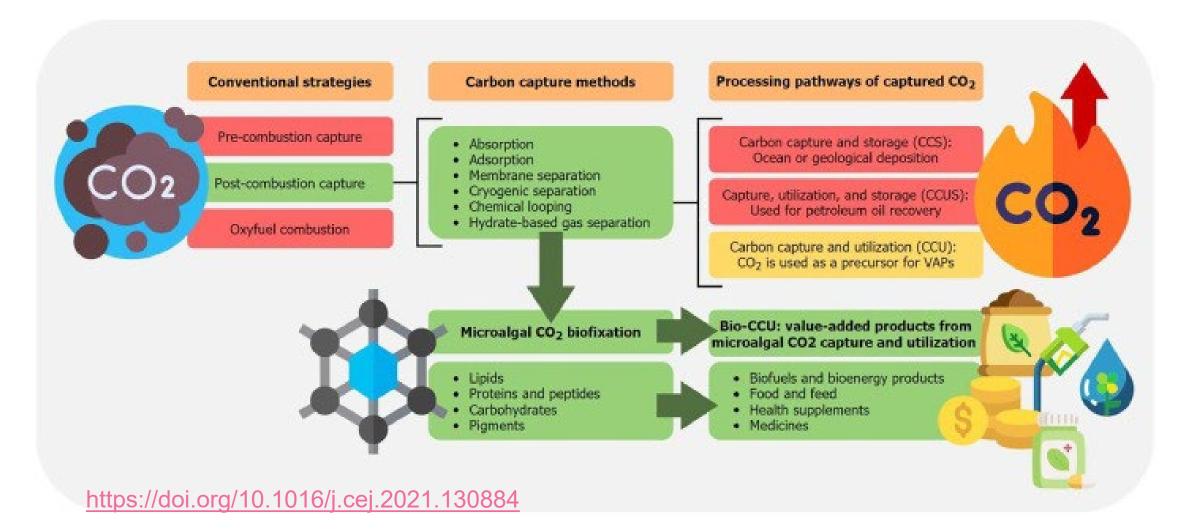




Prof. Dr. Marco Mazzotti Mechanical and Process Engineering



# Photosynthesis: nature-made CCU (carbon capture and utilization) technology



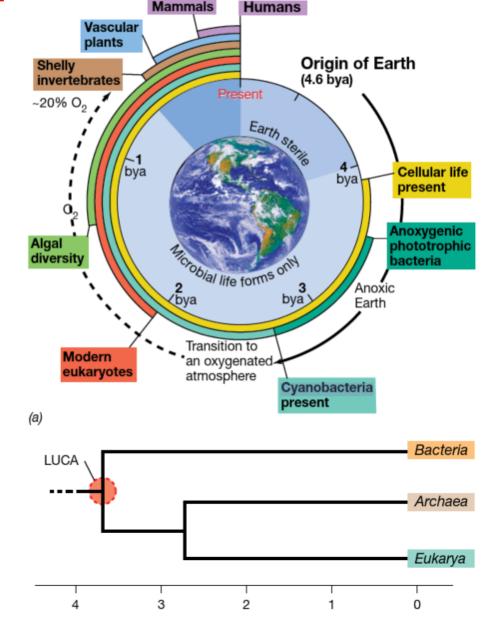


Species	CO <sub>2</sub> %	Aeration rate	CO <sub>2</sub> biofixation rate	Temperature (°C)	Initial pH	Culture medium	Biomass production	References
Botryococcus braunii Scenedesmus sp.	10% mixed with N <sub>2</sub>	0.1 vvm	356 mg/L/day	20	-	BG11	0.41 g/L	[117]
	20% mixed with N <sub>2</sub>	0.1 vvm	532 mg/L/day	20	-	BG11	0.26 g/L	
	10% mixed with N <sub>2</sub>	0.1 vvm	347 mg/L/day	20	-	BG11	0.90 g/L	
	20% mixed with N <sub>2</sub>	0.1 vvm	2177 mg/L/ day	20	-	BG11	1.95 g/L	
Heynigia riparia SX01	0.03% (Ambient air)	0.13 vvm	0.27 g/L/day	28	8	BG-11	1.28 g/L	[118]
	5% mixed with air	0.13 vvm	0.37 g/L/day	28	8	BG-11	2.37 g/L	
	10% mixed with air	0.13 vvm	0.46 g/L/day	28	8	BG-11	2.76 g/L	
	15% mixed with air	0.13 vvm	0.71 g/L/day	28	8	BG-11	3.28 g/L	
Chlorella vulgaris ESP-31 (wild type)	Simulated flue gas containing 25% CO <sub>2</sub>	0.1 vvm	53.35 mg/L/ day	40	7.4	BG-11	0.15 g/L	[119]
Chlorella vulgaris ESP-31 (mutant 283)	Simulated flue gas containing 25% CO <sub>2</sub>	0.1 vvm	272.06 mg/L/ day	40	7.4	BG-11	0.78 g/L	
Chlorella vulgaris ESP-31 (mutant 359)	Simulated flue gas containing 25% CO <sub>2</sub>	0.1 vvm	194.03 mg/L/ day	40	7.4	BG-11	0.64 g/L	
Dunaliella salina	Ambient air	0.5 vvm	0.055 g/L/day	24	8	f/2 medium	$\sim 0.22 \text{ g/L}$	[68]
	6% mixed with air	0.5 vvm	0.067 g/L/day	24	8	f/2 medium	~ 0.26 g/L	
	20% mixed with air	0.5 vvm	0.016 g/L/day	24	8	f/2 medium	~ 0.09 g/L	
	20% mixed with N <sub>2</sub> (constant flow rate)	0.5 vvm	0.043 g/L/day	24	8	f/2 medium	~ 0.30 g/L	
	20% mixed with N <sub>2</sub> (gradual increasing CO <sub>2</sub> level)	0.5 vvm	0.106 g/L/day	24	8	f/2 medium	~ 0.16 g/L	
Chlorella vulgaris P12	2% mixed with air	0.4 vvm	1.5 g/L/day	30	7	Synthetic medium	6.90 g/L	[120]
	6% mixed with air	0.4 vvm	2.29 g/L/day	30	7		10 g/L	
	10% mixed with air	0.4 vvm	1.93 g/L/day	30	7		8.60 g/L	
Chlorella sp.	Flue gas containing 10% $CO_2$	0.5 vvm	261 mg/L/day	28	8.1	Domestic wastewater + poultry waste	1.20 g/L	[121]
Scenedesmus obtusiusculus	Flue gas containing 4–5% CO <sub>2</sub>	-	111.4 mg/L/ day	28	8	BG-11	1.09 g/L	[122]
Chlorella vulgaris (ISC-23)	6% mixed with air	0.5 vvm	3.222 g/L/day	27	7.4	BG11	14.30 g/L	[123]
Chlorella sp. LAMB 31 (high- CO2 tolerant strain)	40% mixed with air	-	0.144 g/L/day	26	6	BG11	~ 1 g/L	[124]
Chlorella sp. LAMB 122 (high-CO2 non-tolerant strain)	40% mixed with air	-	0.017 g/L/day	26	6	BG11	$\sim 0.32~{\rm g/L}$	
Chlorella sp. C-1 (control set)	Ambient air	0.5 vvm	0.357 g/L/day	30	7–8	3N-BBM	1.22 g/L	[125]
Chlorella sp. E-1	Flue gas containing 10%	0.5 vvm	0.469 g/L/day	30	7–8	3N-BBM	1.69 g/L	
(experimental set)	$CO_2$							

## Cyanobacteria







bya

#### A MICROBIAL PLANET

- Estimated Earth age = 4.6 billion years
- Microbial cells appeared 3.8-4.3 bya
- In first 2 billion y, earth was anoxic
- Only microorganisms with anerobic metabolisms
- Phototropic organisms (harvest energy from sun) appeared within the first billion years
- The 1<sup>st</sup> of these were anoxygenic (non-oxygen producing)
- Nearly 1 billion years later, cyanobacteria evolved
- Cyanobacteria are oxygenic photoautotrophs and started the process of oxygenating the atmosphere
- After oxygenation, multicellular organisms began to evolve, eventually plants and animals in the last half billion years
- 80% of life's history was exclusively microbial

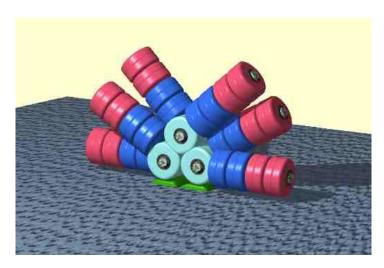
Brock Biology of Microorganisms, Global Edition

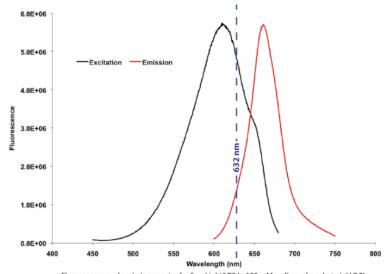
## **Cyanobacteria (formerly called blue-green algae)**

### Gram negative

- Chromophores: Chlorophyll a, phycobilins (phycocyanin and allophycocyanin), carotenoids
- Light absorption: Chlorophyll a absorbs blue and red, phycobilins absorb green and orange – combination targets broad visible spectral range
- Light harvesting complex called phycobilisomes
- Fixate carbon, produce oxygen (oxygenic photosynthesis)

## The layout of protein subunits in a phycobilisome





Fluorescence and emission spectra for SureLight® P3 in 100 mM sodium phosphate (pH 7.2), 1mM EDTA, and 1mM sodium azide. Scans were normalized to equalize peak heights.



# Microbially induced calcite precipitation (MICP)

- Different mechanisms, of which photosynthesis is one
- CO<sub>2</sub> and HCO<sub>3</sub>- uptake by photosynthesis increases local pH
- Shifts equilibrium to favor CO<sub>3</sub><sup>2-</sup>
- Cyanobacteria EPS can bind Ca<sup>+2</sup>
- EPS acts a nucleation site for CaCO<sub>3</sub> crystal formation

### Other mechanisms:

- Urea hydrolysis
- Ammonification
- Denitrification
- Sulfate reduction
- Methane oxidation



## Features of cyanobacteria relevant to CCS

- Thrive at high CO<sub>2</sub> levels (e.g., flue gas)
- Halophilic can be cultured in marine waters or other high salinity waters (e.g., brine from petroleum refining)
- Thermophilic tolerate high temperatures (e.g., flue gas)
- Can enrich the amount of CO<sub>2</sub> up to 1000-fold the surrounding media
- Article describes calcification by cyanobacteria as "as a niche technology, preferably linked to small coal-fired power plants, natural gas systems, municipal solid waste combustion, and CO<sub>2</sub>-emitting industries such as cement manufacture, and iron and steel production. If nation-wide distributions of such units were to be deployed in countries such as the U.S.A., China and India, the impact in mitigation of global greenhouse gas emissions could be enormous"



#### **Abstract**

Natural ecosystems offer efficient pathways for carbon sequestration, serving as a resilient approach to remove CO<sub>2</sub> from the atmosphere with minimal environmental impact. However, the control of living systems outside of their native environments is often challenging. Here, we engineered a photosynthetic living material for dual CO<sub>2</sub> sequestration by immobilizing photosynthetic microorganisms within a printable polymeric network. The carbon concentrating mechanism of the cyanobacteria enabled accumulation of CO<sub>2</sub> within the cell, resulting in biomass production. Additionally, the metabolic production of OH<sup>-</sup> ions in the surrounding medium created an environment for the formation of insoluble carbonates via microbially-induced calcium carbonate precipitation (MICP). Digital design and fabrication of the living material ensured sufficient access to light and nutrient transport of the encapsulated cyanobacteria, which were essential for long-term viability (more than one year) as well as efficient photosynthesis and carbon sequestration. The photosynthetic living materials sequestered approximately 2.5 mg of CO<sub>2</sub> per gram of hydrogel material over 30 days via dual carbon sequestration, with  $2.2 \pm 0.9$  mg stored as insoluble carbonates. Over an extended incubation period of 400 days, the living materials sequestered 26 ± 7 mg of CO<sub>2</sub> per gram of hydrogel material in the form of stable minerals. These findings highlight the potential of photosynthetic living materials for scalable carbon sequestration, carbon-neutral infrastructure, and green building materials. The simplicity of maintenance, coupled with its scalability nature, suggests broad applications of photosynthetic living materials as a complementary strategy to mitigate CO<sub>2</sub> emissions.



- Carbon
- 2. Carbon sequestration
- 3. Photosynthesis
- MICP
- 5. Cyanobacteria
- Hydrogel **last few weeks**
- 7. 3D printing **last week**
- 8. Photosynthetic living materials