# Laboratory of High Pressures

*The head*

Associate prof.

**Vladimir Kutcherov**




**Elena Mukhina**

**Daniil Kudryavtsev**

**PhD, Anton Kolesnikov**

**Alexandr Serovaisky**

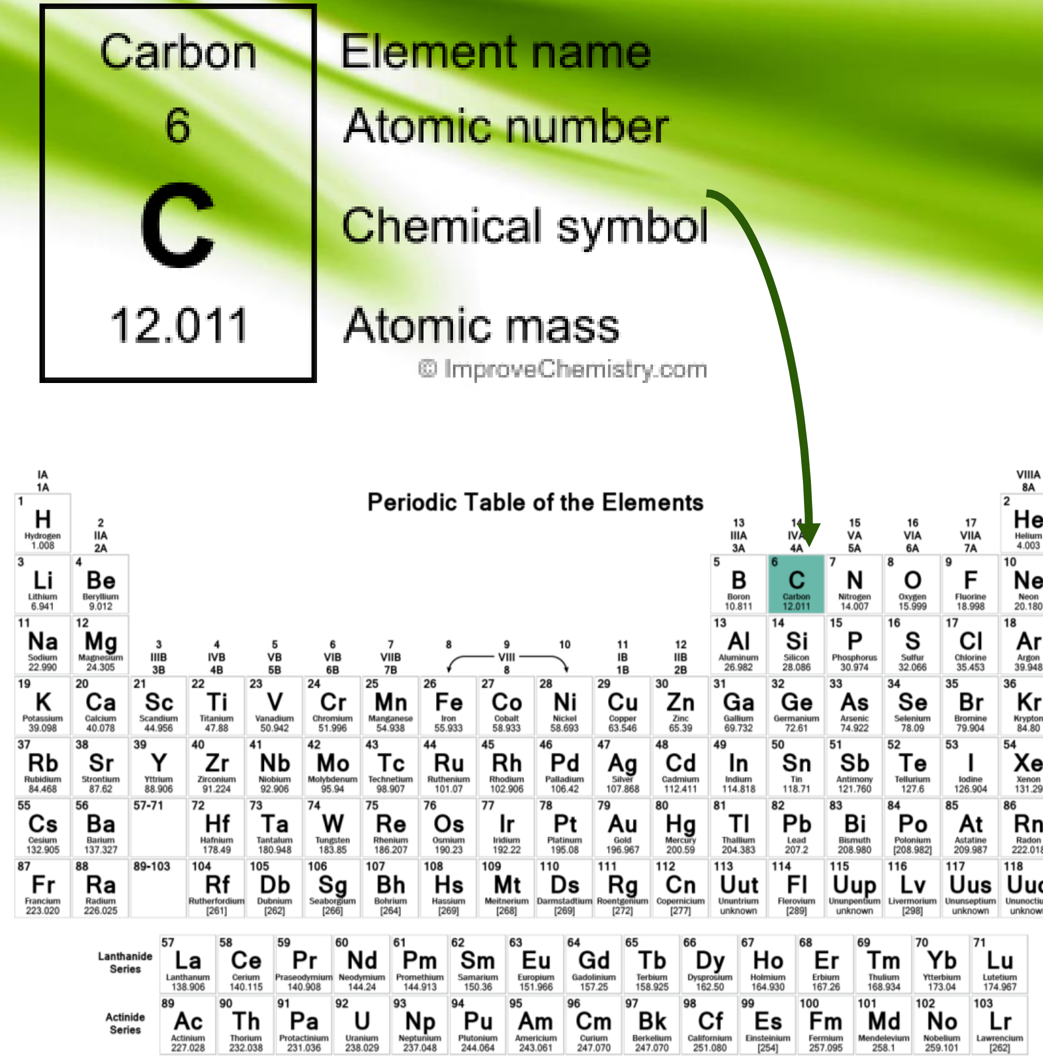
***Research area***

- **High-pressure-temperature experiments**
- **Behavior of hydrocarbons**
- **Planets' interior processes**

# $CO_2$ as part of Global Carbon Cycles

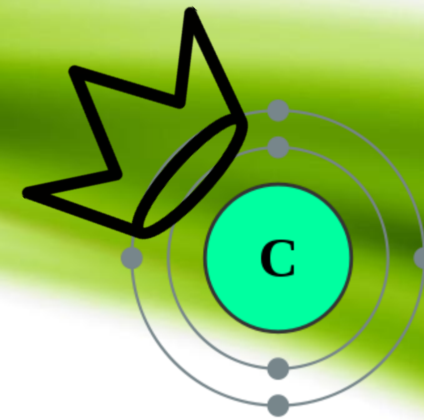
Daniil Kudryavtsev, PhD student
Scientific supervisor: Prof. Vladimir Kutcherov

# Carbon is …

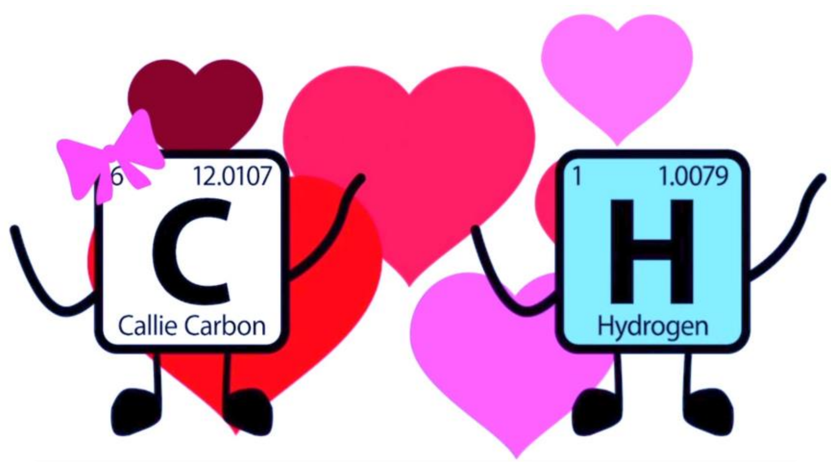



Carbon (Latin: carbo "coal") is a chemical element with symbol C and atomic number 6

# Why carbon is so unique element?

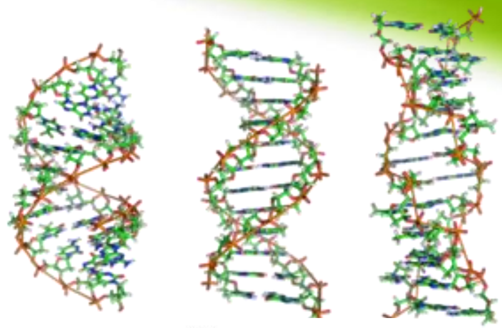


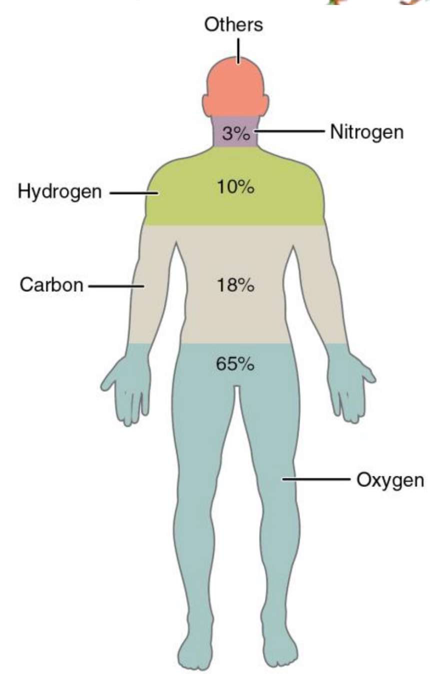

- Carbon is a **king** of the elements!
- **Carbon** atoms can bond to each other to a practically **unlimited degree**!
- Carbon forms more than **10 million** compounds!
- Carbon has the richest chemistry!

# Carbon is a building block of life

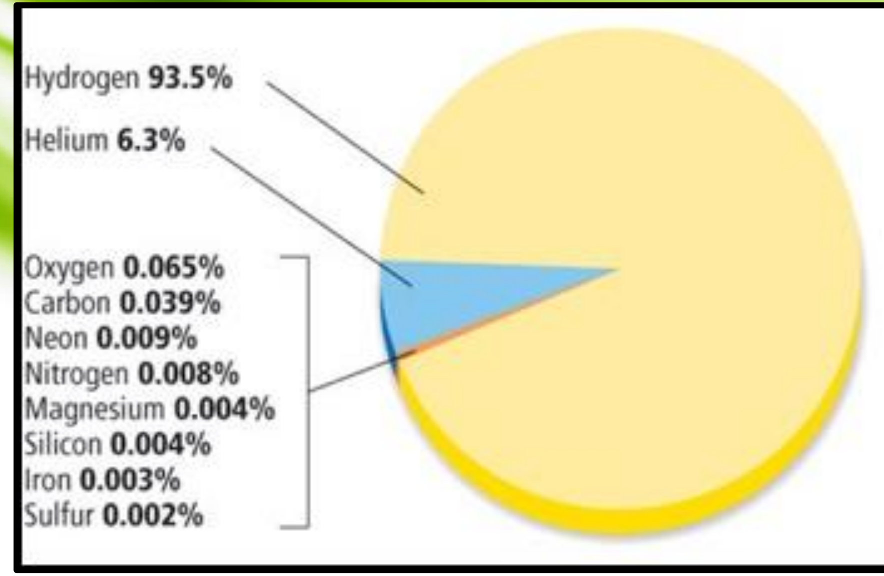
- Carbon is an element found in all living things and without it there would be no life on Earth
- It is the second most abundant element in the human body by mass (about 18.5%) after oxygen
- The carbon atoms in your body were all once part of the carbon dioxide fraction of the atmosphere ☺





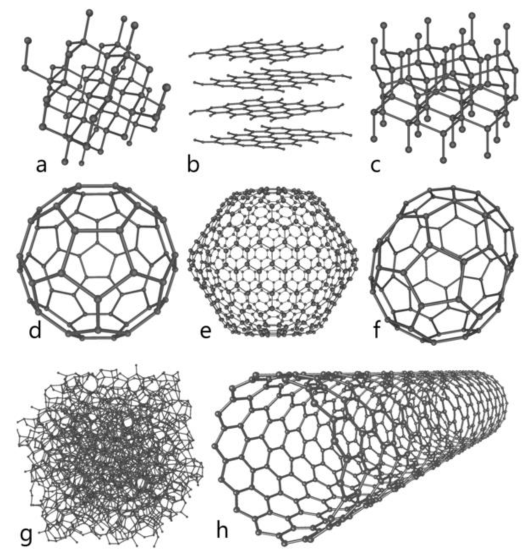
# Some facts about carbon:

- Carbon is **the 15th** most abundant element in the Earth's crust
- Carbon is **the fourth** most abundant element in the universe
- Elemental carbon can take the form of one of the hardest substances (diamond) or one of the softest (graphite).






Around 500 allotropic forms of carbon!



# Distribution of carbon on the Earth

$HCO_3^-$ (36000 Gt) + dissolved $CO_2$ + organic carbon + $CO_3^{2-}$ + partially methane hydrates

$CO_2$ (0.0360% of atmosphere) $CH_4$ (0.00017% => 200 times less than $CO_2$)

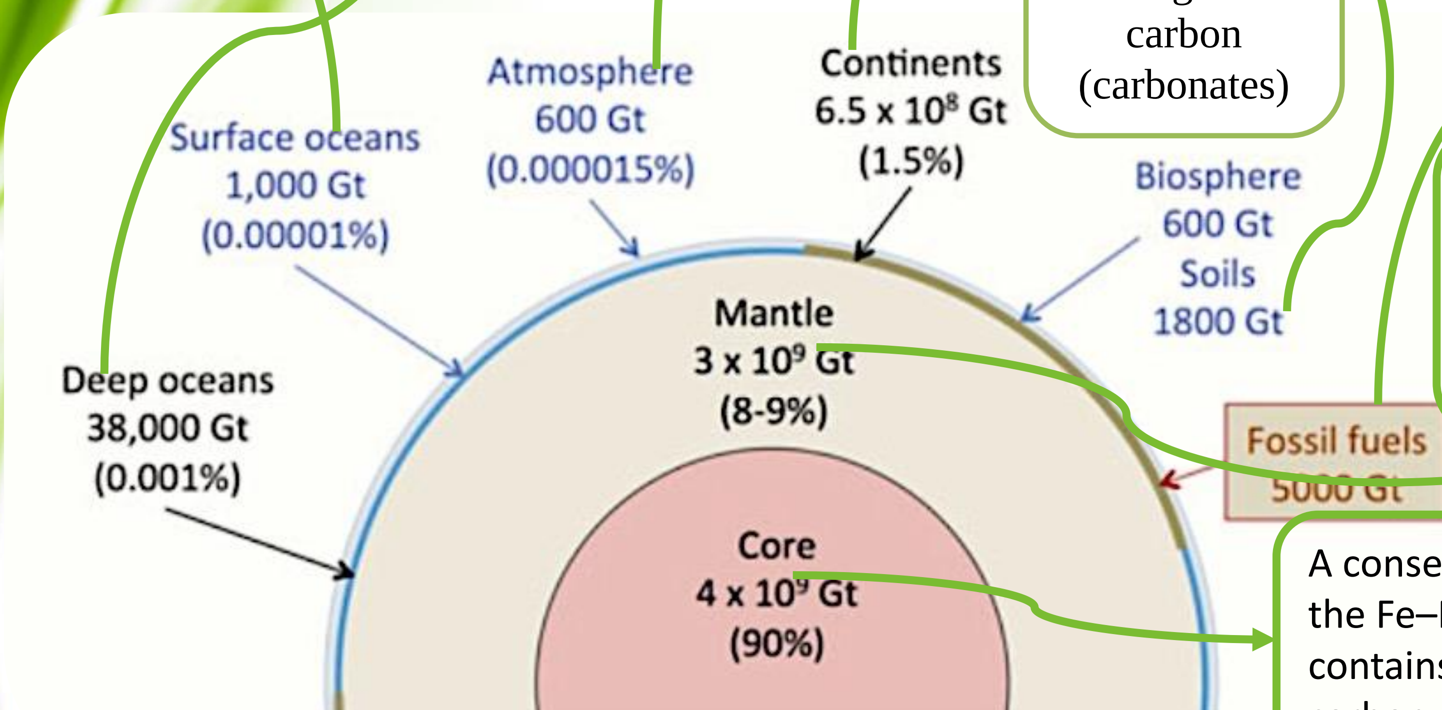
Limestone and dolomite, marble (Ca,Mg) CO3

Crude oil (150 Gt), natural gas (105 Gt), coal (4000 Gt), shale gas (540 Gt)

Organic (soil biota + dead biotic material) and inorganic carbon (carbonates)

Silicate compounds of Mg, Fe, Ca, and Al, contain about 0.01% (100 ppm) carbon by weight

A conservative estimate is that the Fe–Ni alloy in the core contains about 0.2% by weight carbon.




Donald J. DePaolo , 2015

This is a line.
This is a linear process.

This is a cycle.
It is a circular pathway and has no clear start and finish.

Why cycle?

key to make Earth capable of sustaining life

# Global Carbon Cycle

Biological/Physical (Short-term) ($10^{16}$-$10^{17}$ gram/year)

The Geological (Long-term) ($10^{14}$-$10^{15}$ gram/year)

Carbon molecules cycle, meaning that they move through the land, the air, and the water.

Follow the simpe example of carbon trip!

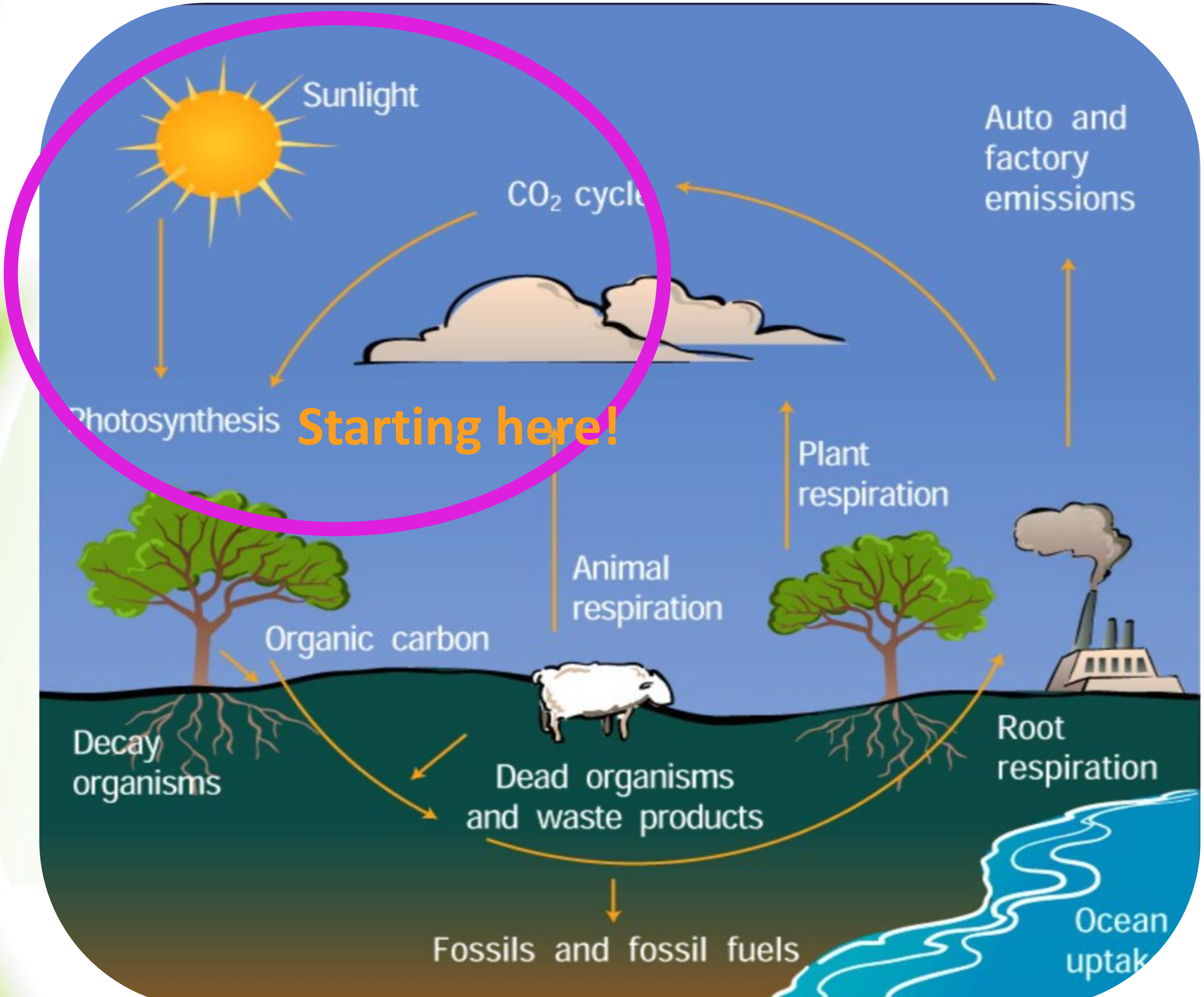
Cellulose $(C_6H_{10}O_5)_n$

burning


photosynthesis

harvesting

# Short-term carbon cycle

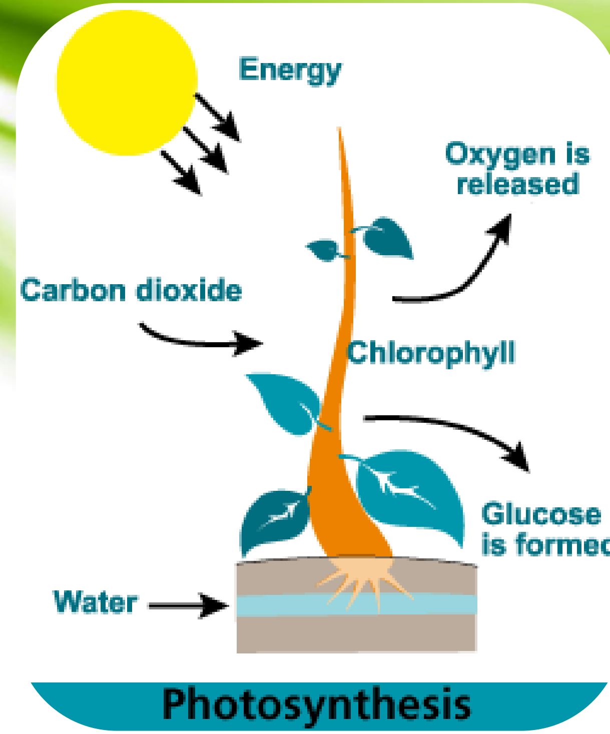



R. Johnson, 2010

Plants use light energy from the Sun and $CO_2$ from the air for the process of photosynthesis. Producers absorb carbon dioxide from the air to make molecules of glucose (food) which includes carbon atoms.

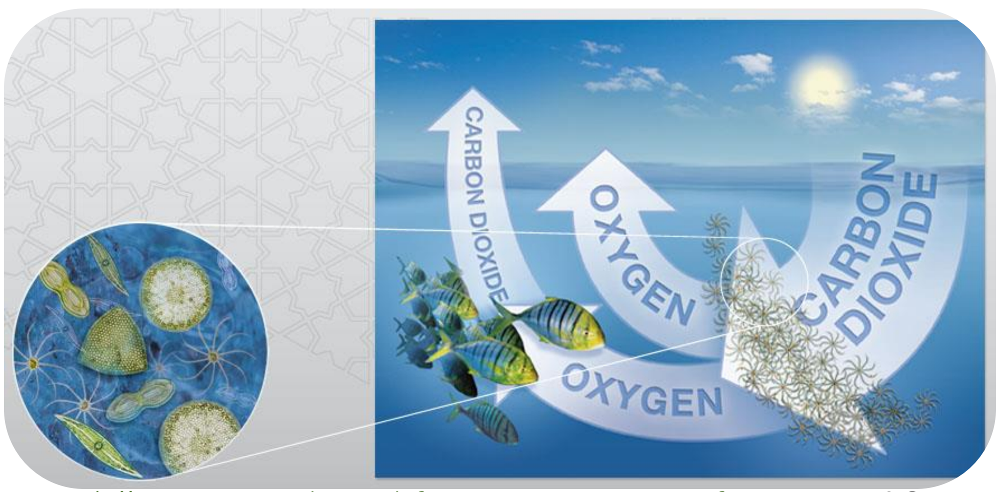
# Photosynthesis:

$$\underset{\text{Carbon dioxide}}{6CO_2} + \underset{\text{Water}}{6H_2O} \xrightarrow{\text{Light}} \underset{\text{Sugar}}{C_6H_{12}O_6} + \underset{\text{Oxygen}}{6O_2}$$



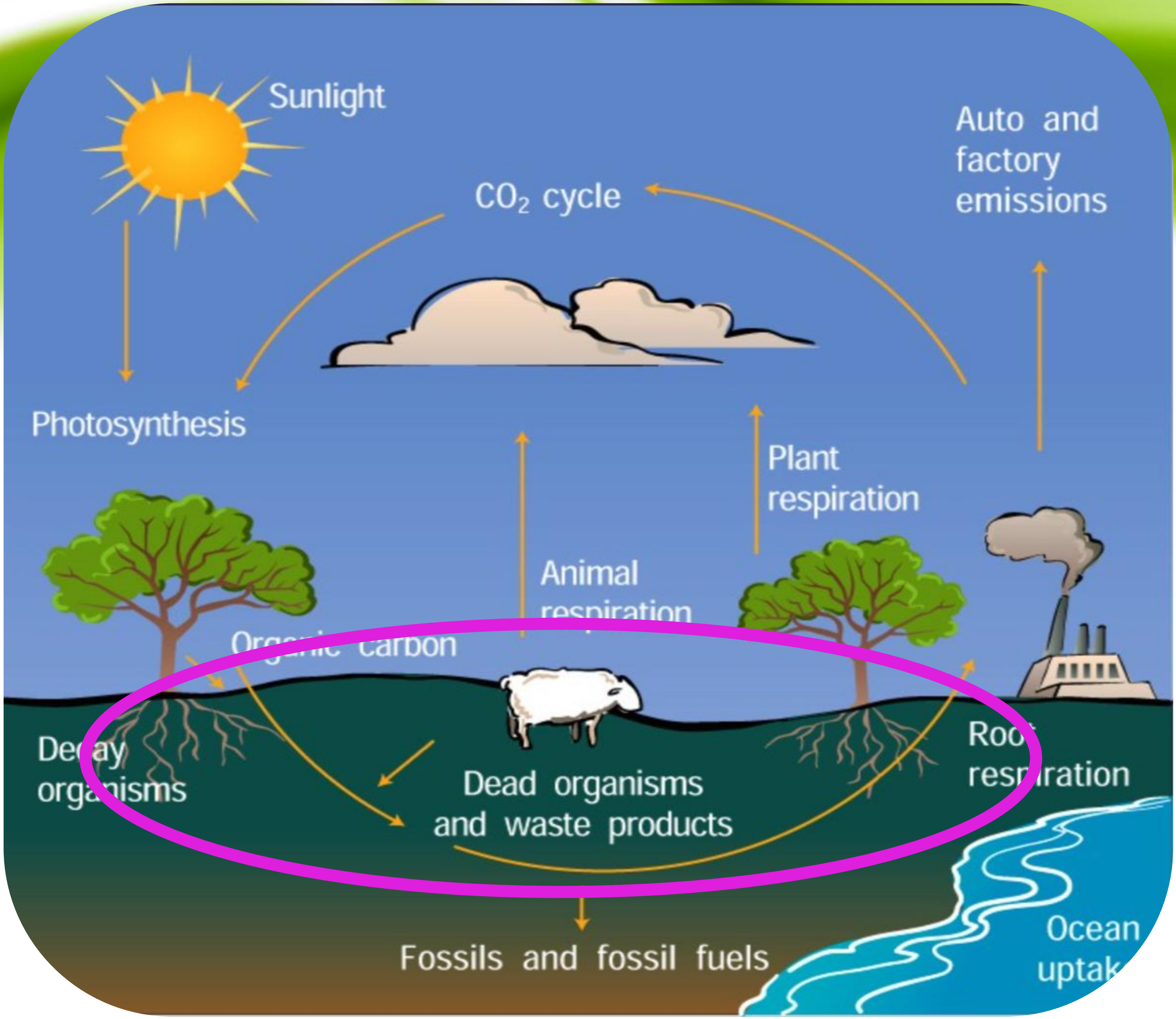

By Riyasachdeva250 (Own work) [CC BY-SA 4.0 (https://creativecommons.org/licenses/by-sa/4.0)], via Wikimedia Commons

After plants make glucose molecules, they change these molecules into molecules of starches, proteins, and fats, all which also contain carbon atoms—carbon atoms that were once part of the $CO_2$ in the air.



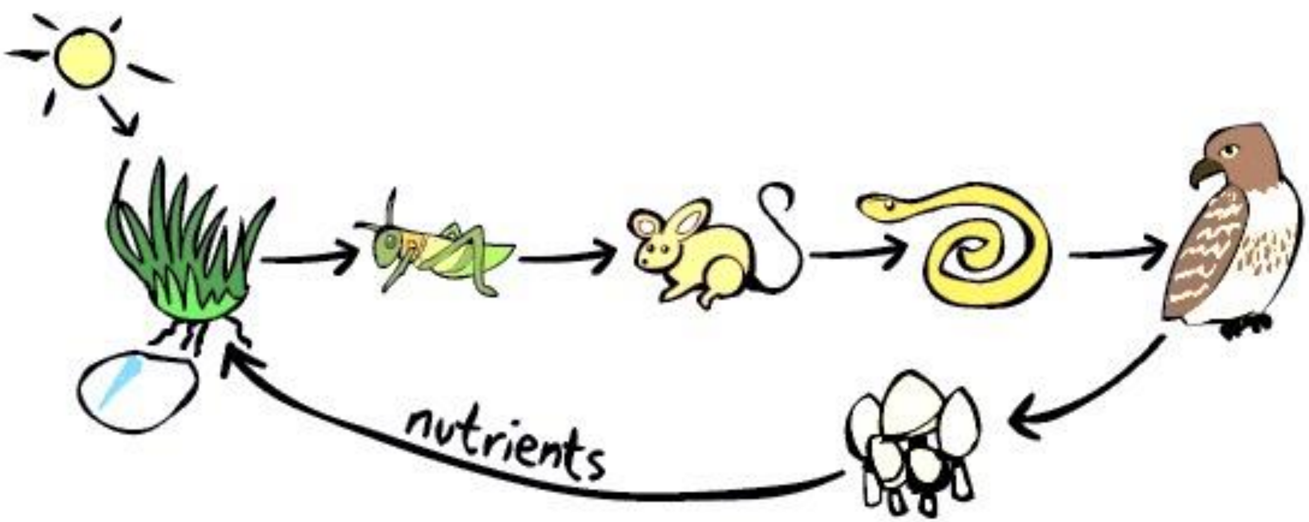

(Illustration adapted from A New Wave of Ocean Science, U.S. JGOFS.)

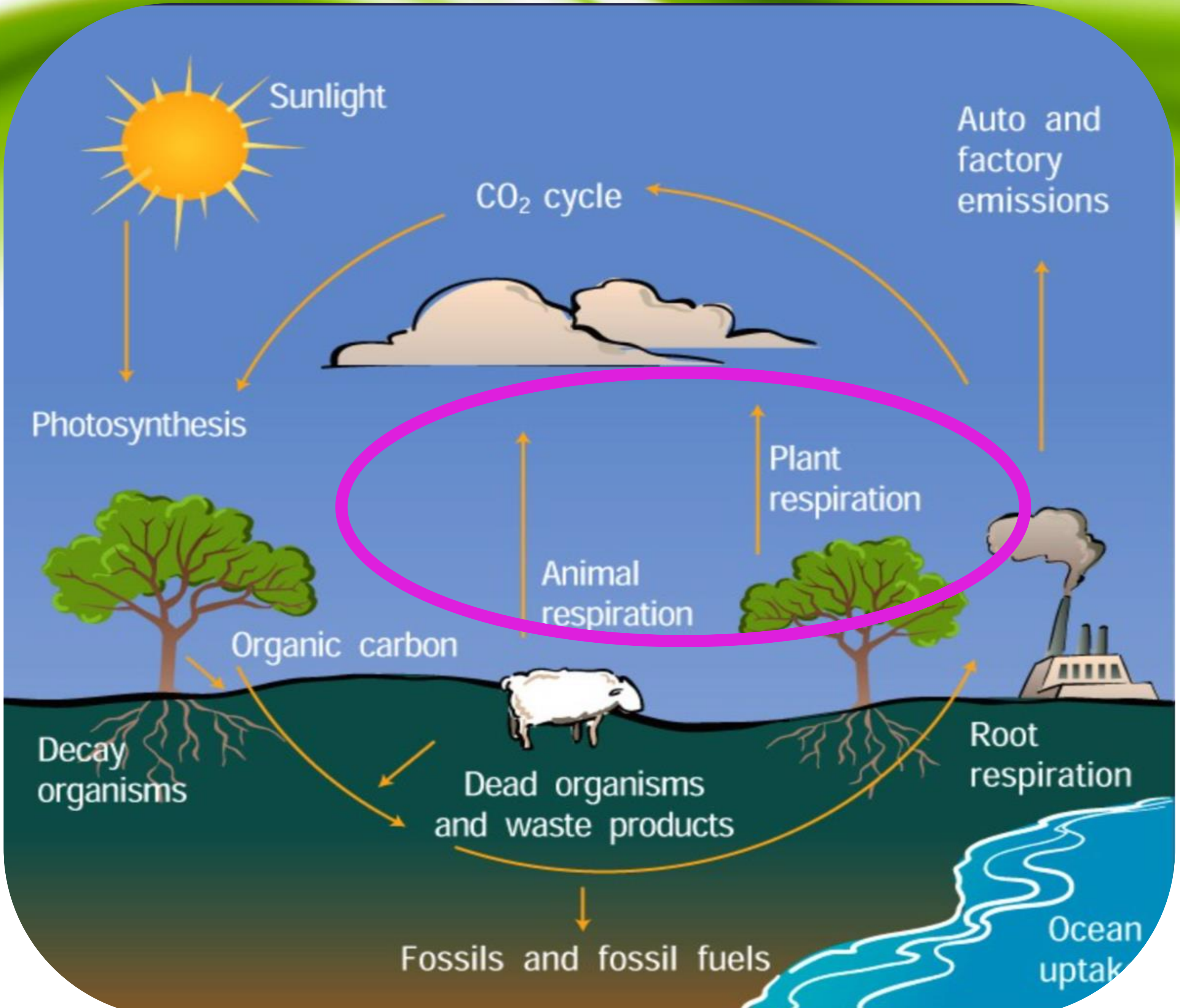
By photosynthesis, tiny producers in the ocean called phytoplankton, absorb a massive amount of dissolved carbon dioxide from the water and release oxygen into the atmosphere.




R. Johnson, 2010

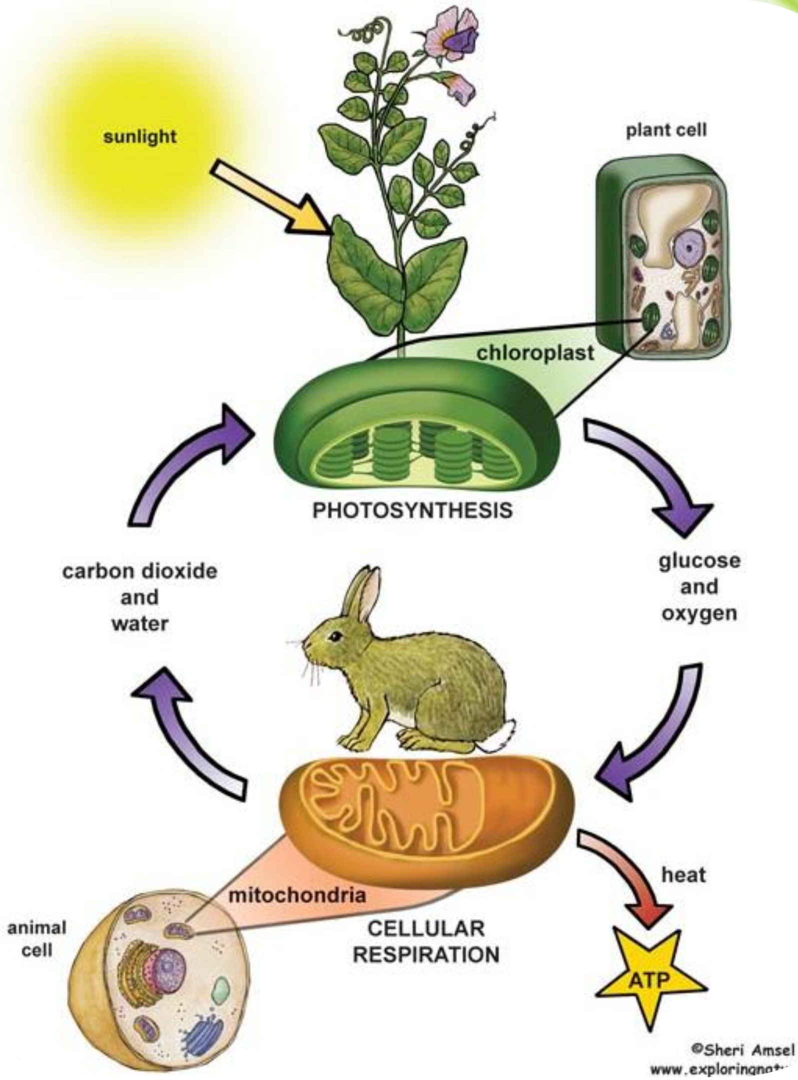

HERBIVORES
These are animals
This includes leaves
mainly meat.
OMNIVORES
These are animals able to eat plants AND animals.
Some omnivores are:
•humans
•most bears
•raccoons
•most primates (apes & monkeys)
•seagulls & other birds
Basic Photosynthesis
DECOMPOSERS
They consume (eat) dead plants & animals and decomposes them - reduces them to simpler forms of matter.
PRIMARY DECOMPOSERS
Fungi & Bacteria

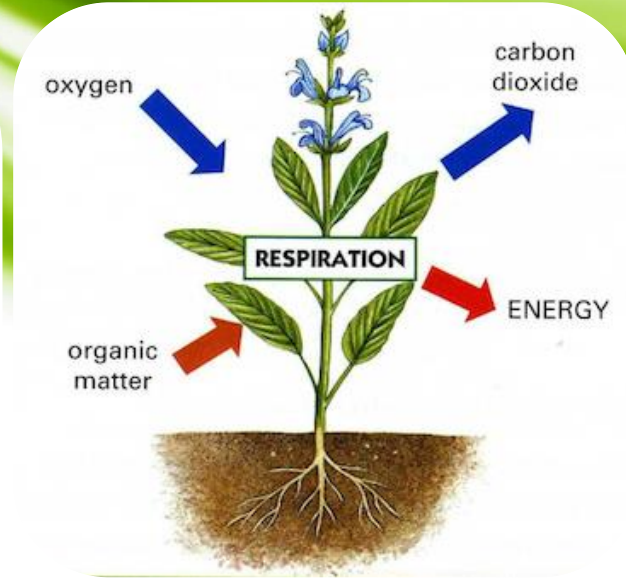

nutrients






R. Johnson, 2010



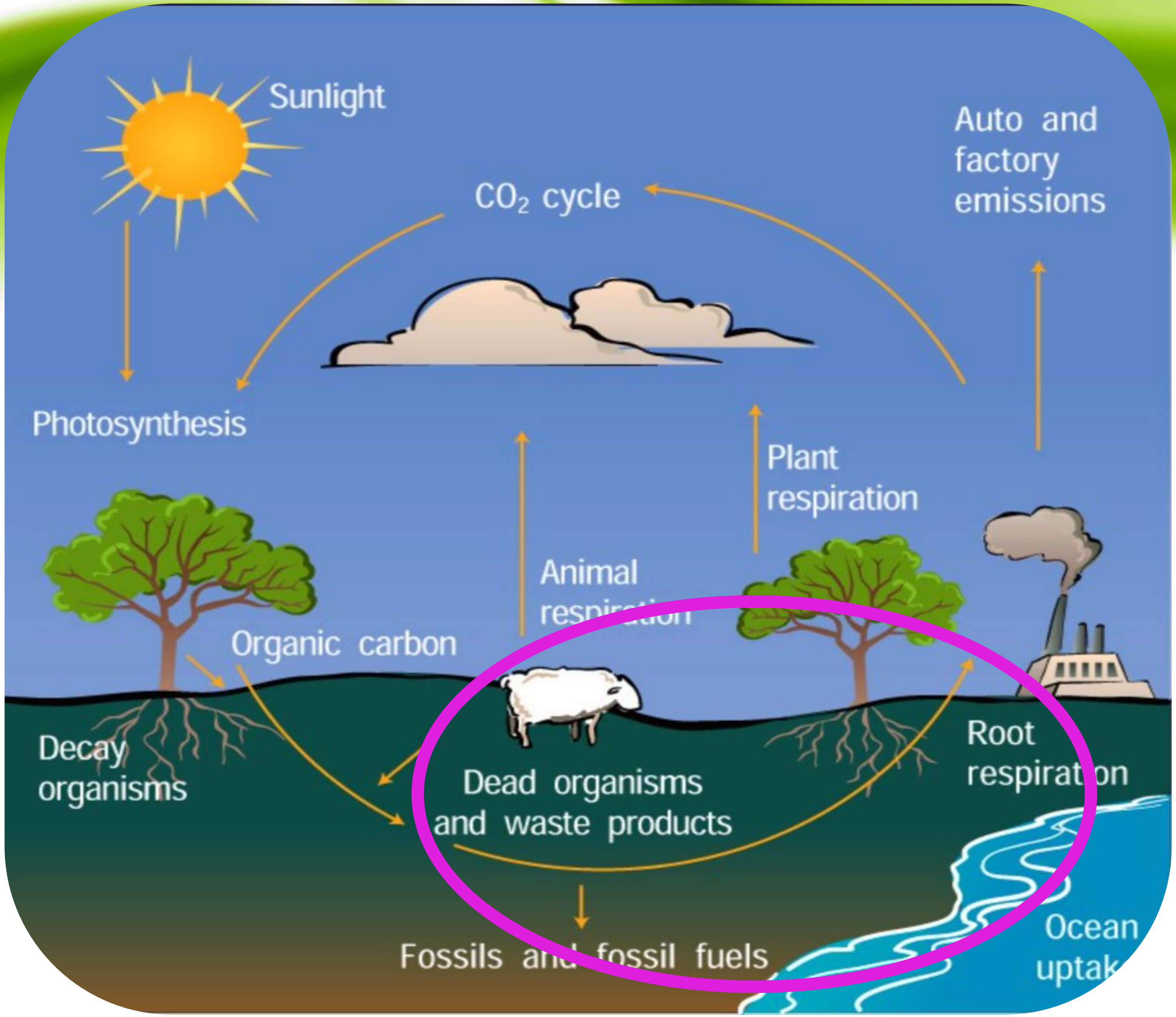

Courtesy of the 2007 IPCC report


Courtesy of the 2007 IPCC report

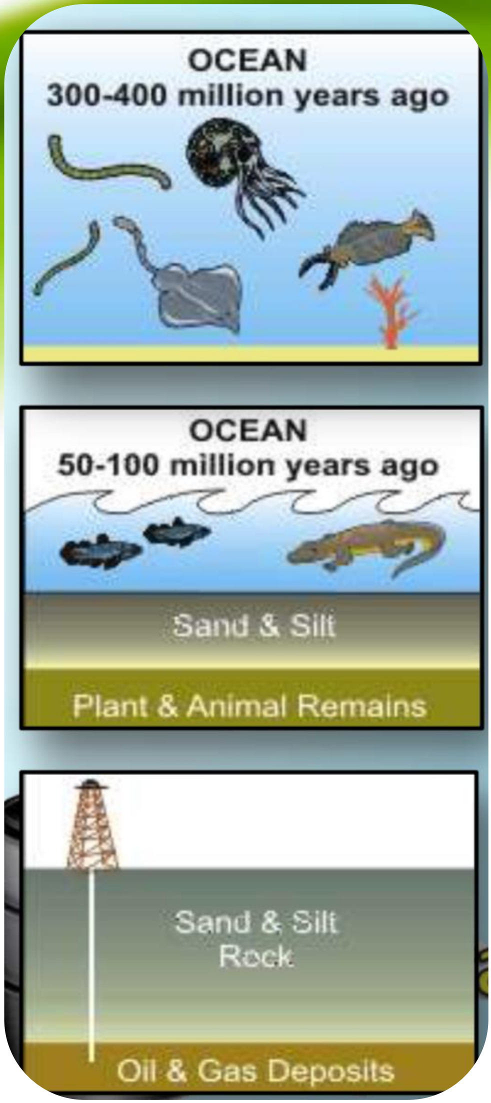
What goes in | What comes out

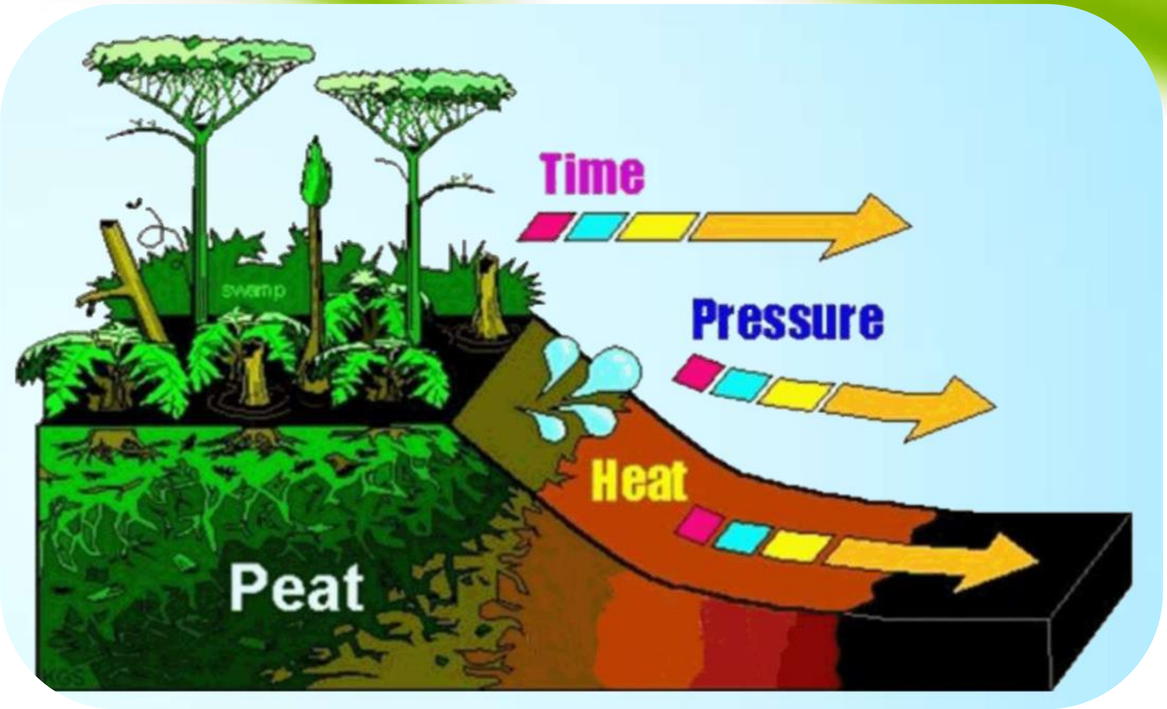
$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O + \text{Energy}$$

- $C_6H_{12}O_6$: Glucose (food)
- $O_2$: Oxygen (in air we breathe)
- $CO_2$: Carbon dioxide (in air we exhale)
- $H_2O$: Water
- Energy: Energy that keeps our bodies running




R. Johnson, 2010

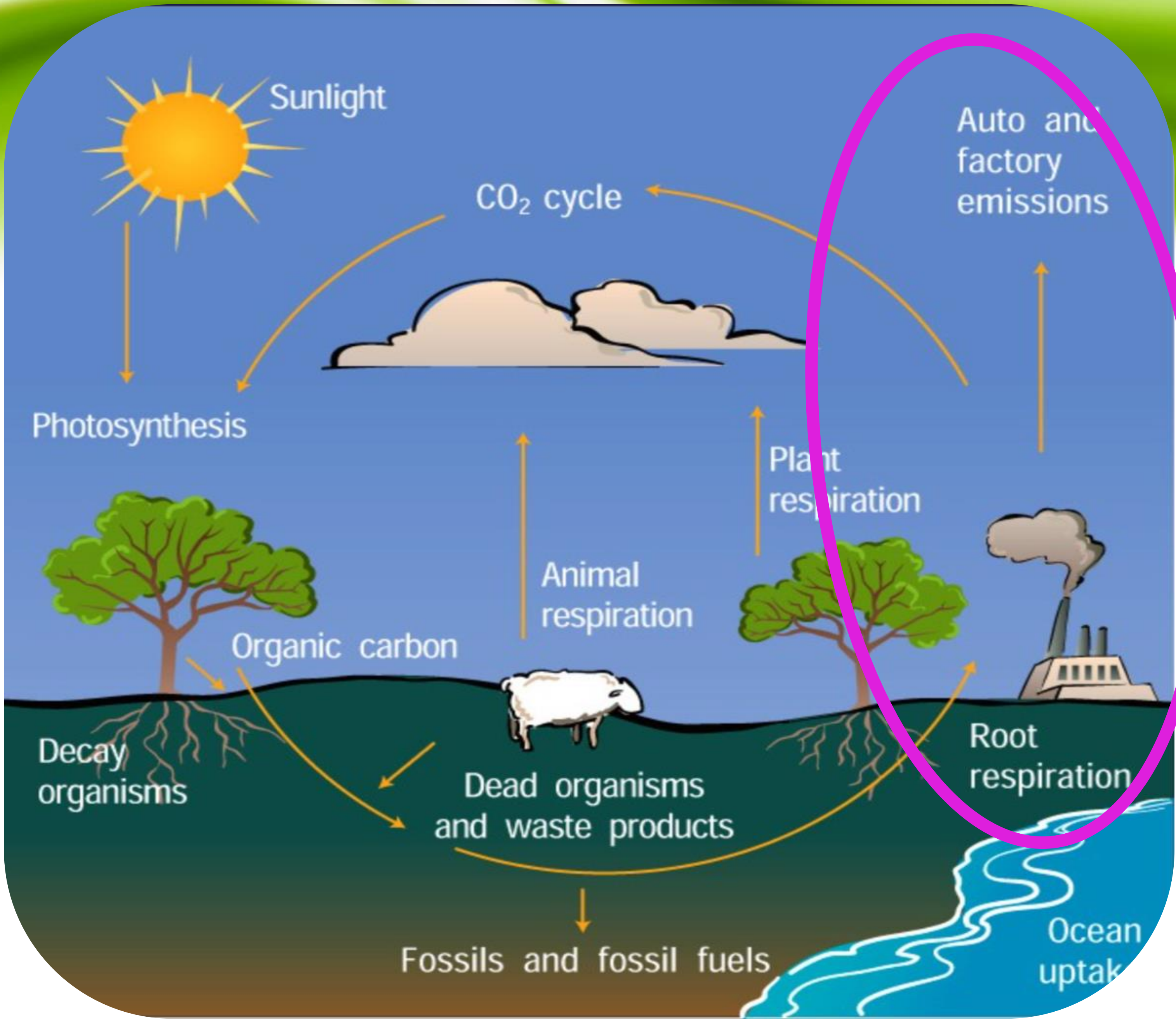



S. Greb, Kentucky Geological Survey.

Oil & gas formation Coal & Peat formation

# Fossilization




R. Johnson, 2010

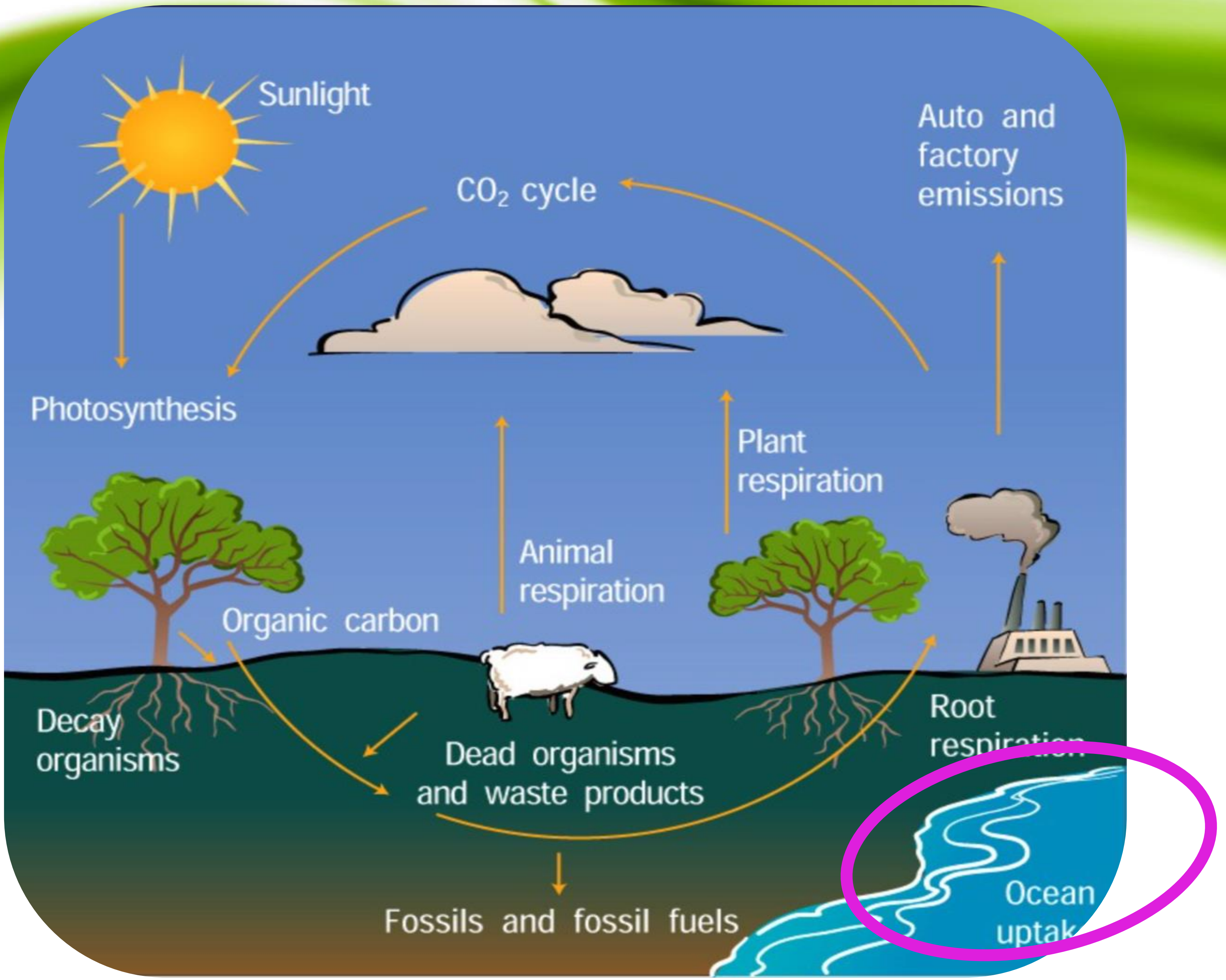
# Combustion

HydroCarbon      Carbon Dioxide

$$CH + O_2 \rightarrow CO_2 + H_2O$$

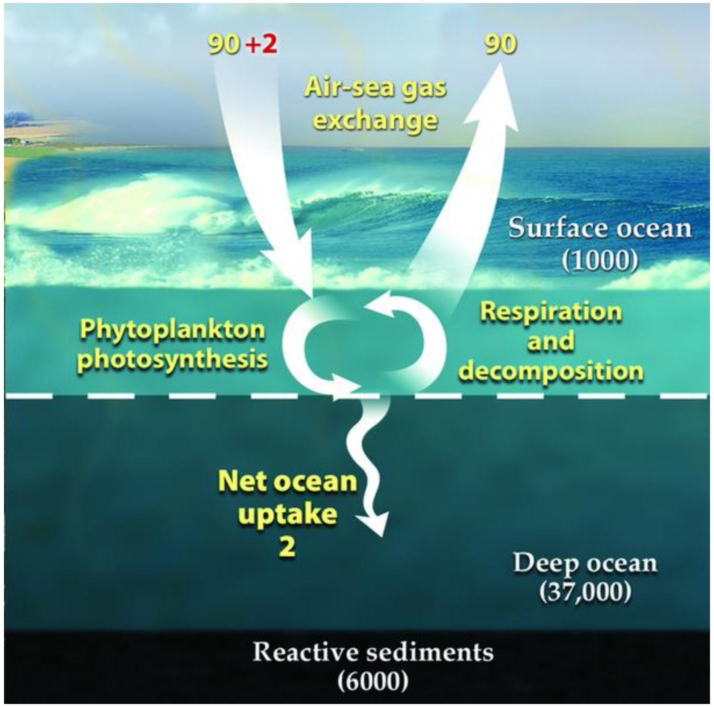
Oxygen      Water


## Combustion



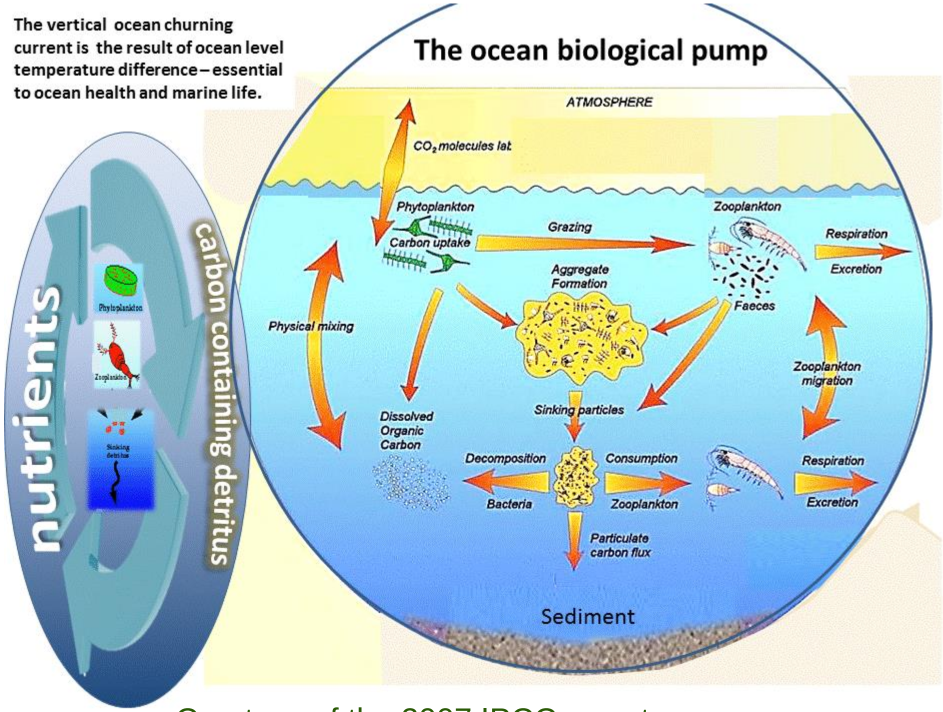

R. Johnson, 2010


https://serc.carleton.edu/eslabs/carbon/index.html

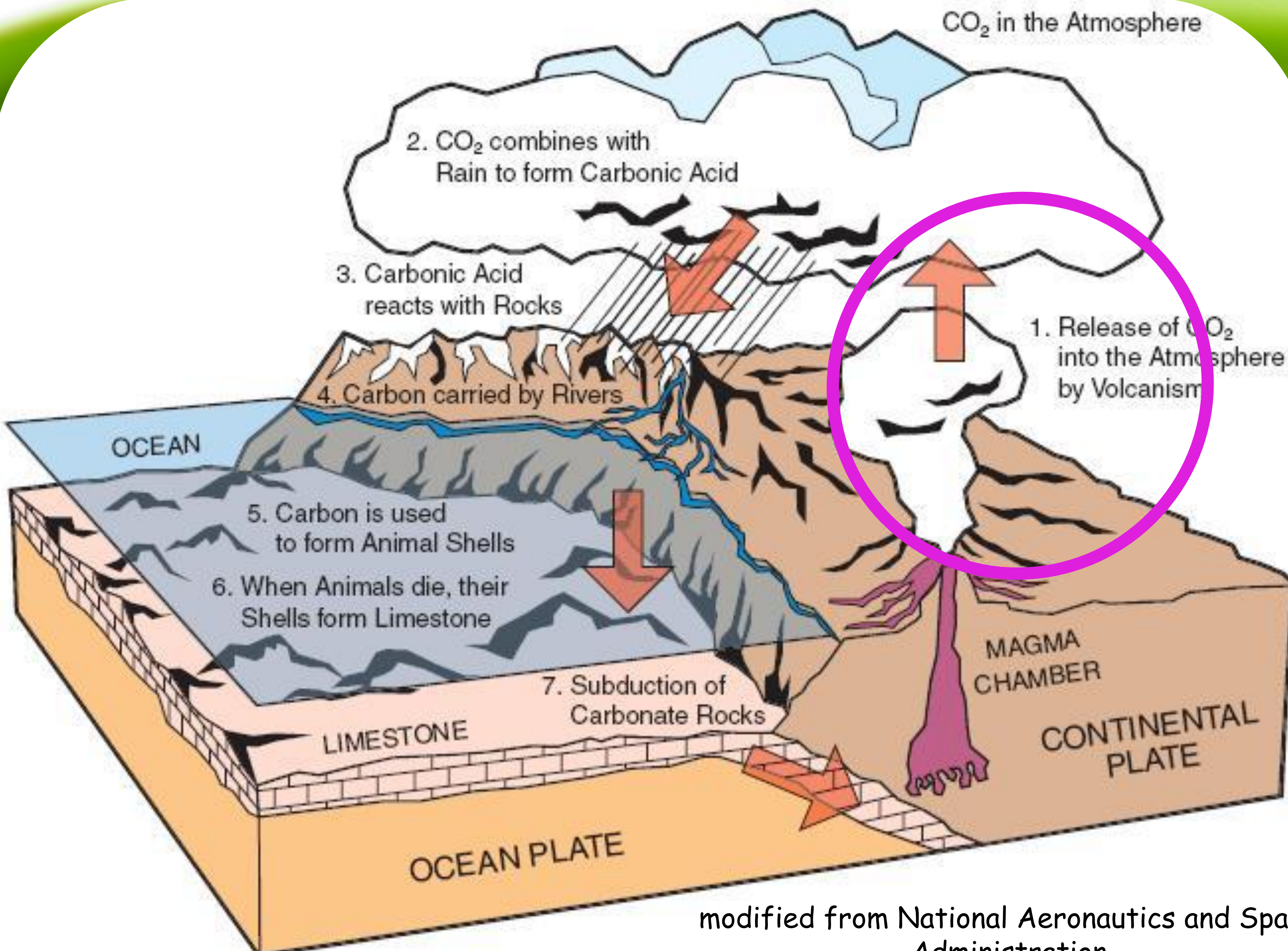



ram adapted from U.S. DOE, Biological and Environmental Research Information System.

The vertical ocean churning current is the result of ocean level temperature difference – essential to ocean health and marine life.

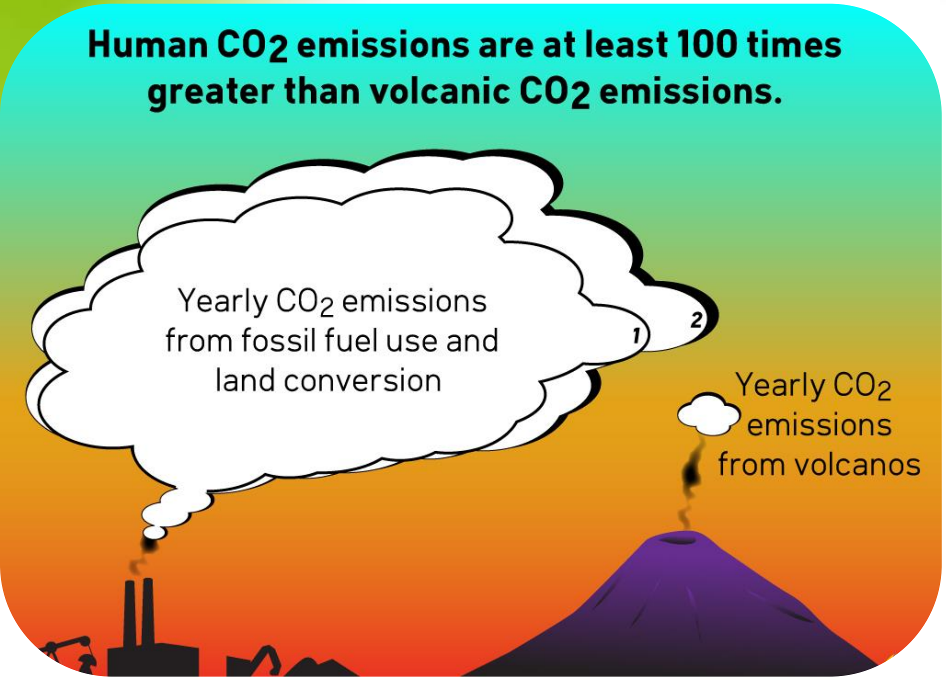



Courtesy of the 2007 IPCC report




modified from National Aeronautics and Space Administration

# What about geology?




Gerlach 2011

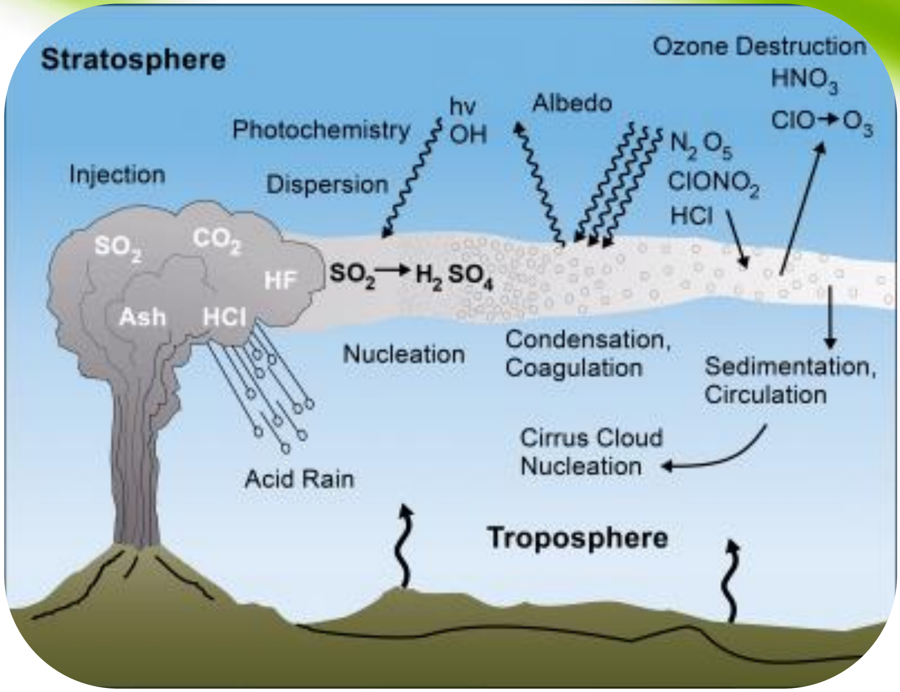
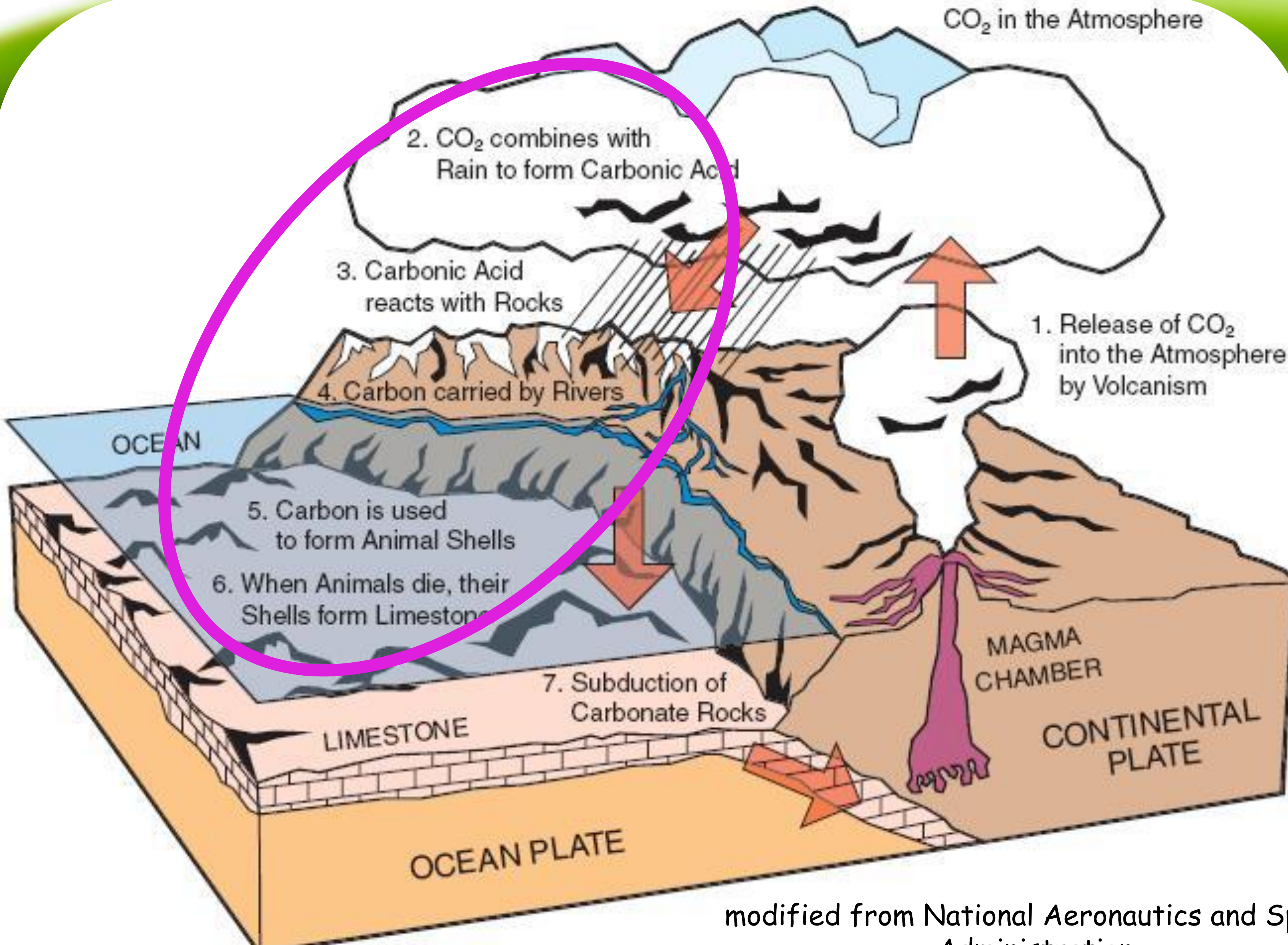



figure modified from Richard Turco in American Geophysical Union Special Report: Volcanism and Climate Change, May 1992

# Volcanism



modified from National Aeronautics and Space Administration

# What about geology?

$$CO_2 + H_2O = H_2CO_3$$

$H_2CO_3 + H_2O$ + silicate minerals -> $HCO_3^-$ + cations ($Ca^{++}$, $Fe^{++}$, $Na^+$, etc.) + clays

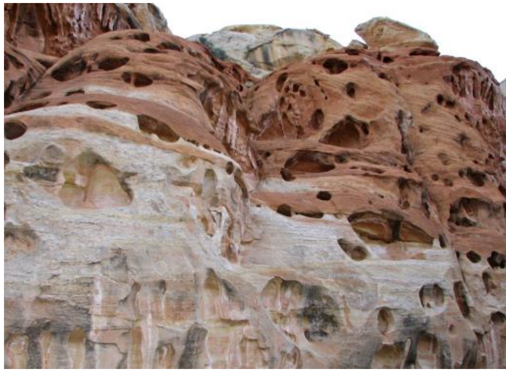
$$Ca^{++} + 2HCO_3^- \rightarrow CaCO_3 + CO_2 + H_2O$$

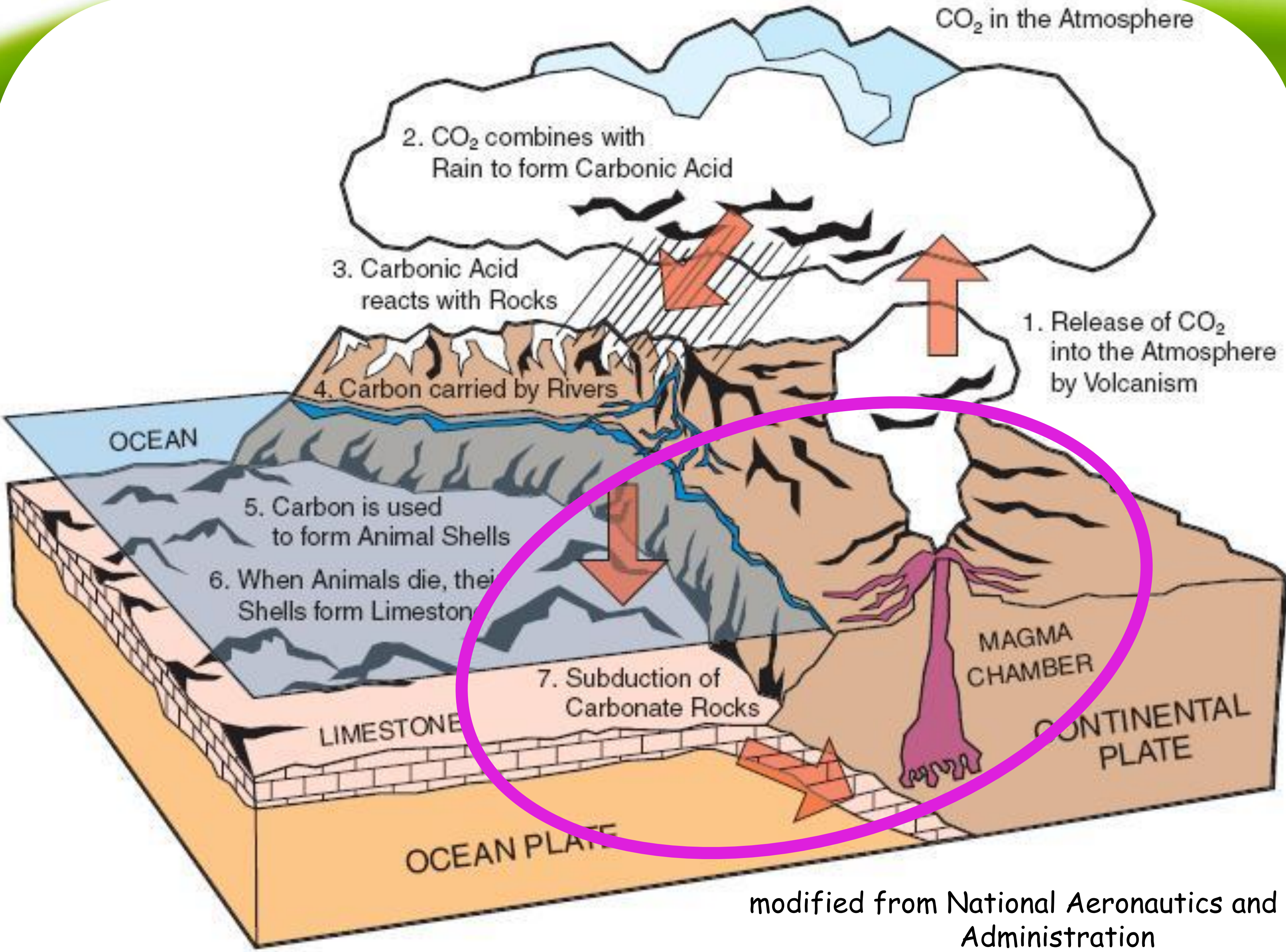
The carbon is now stored
In the seafloor!

$$CaCO_3 + SiO_2 \rightarrow CO_2 + CaSiO_3$$

Some of this carbon is returned to the atmosphere via metamorphism

# Weathering



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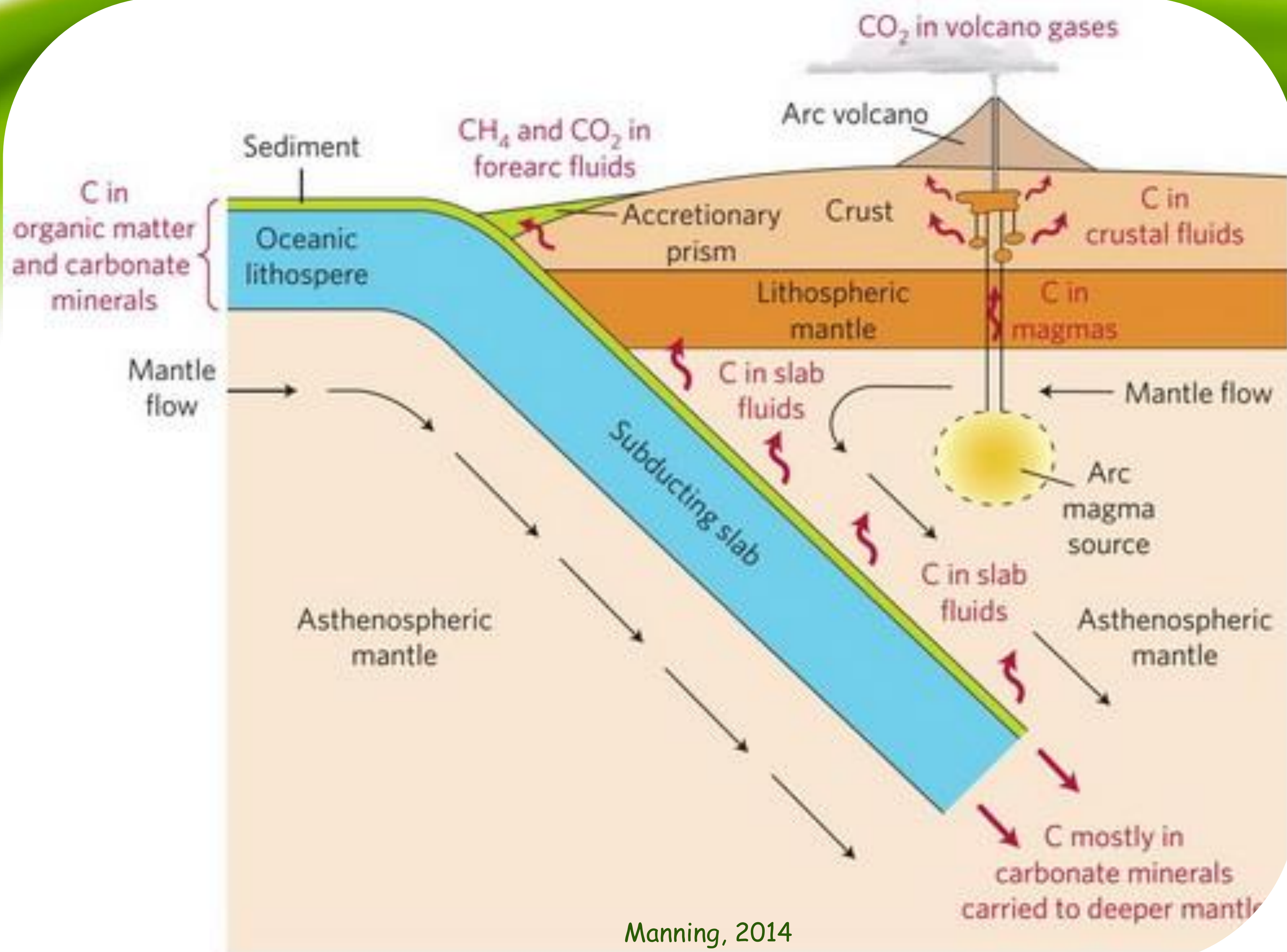
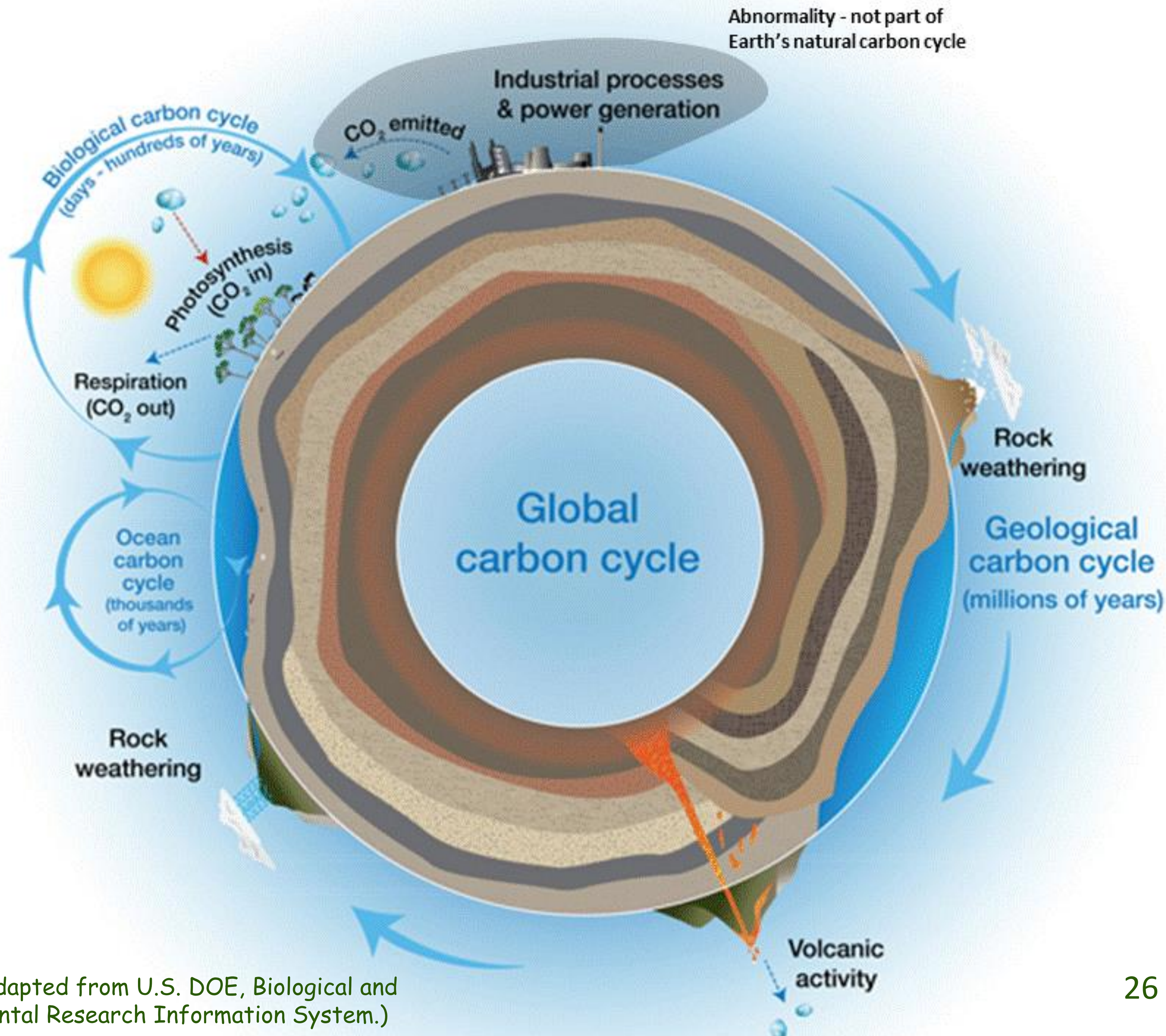
# What about geology?

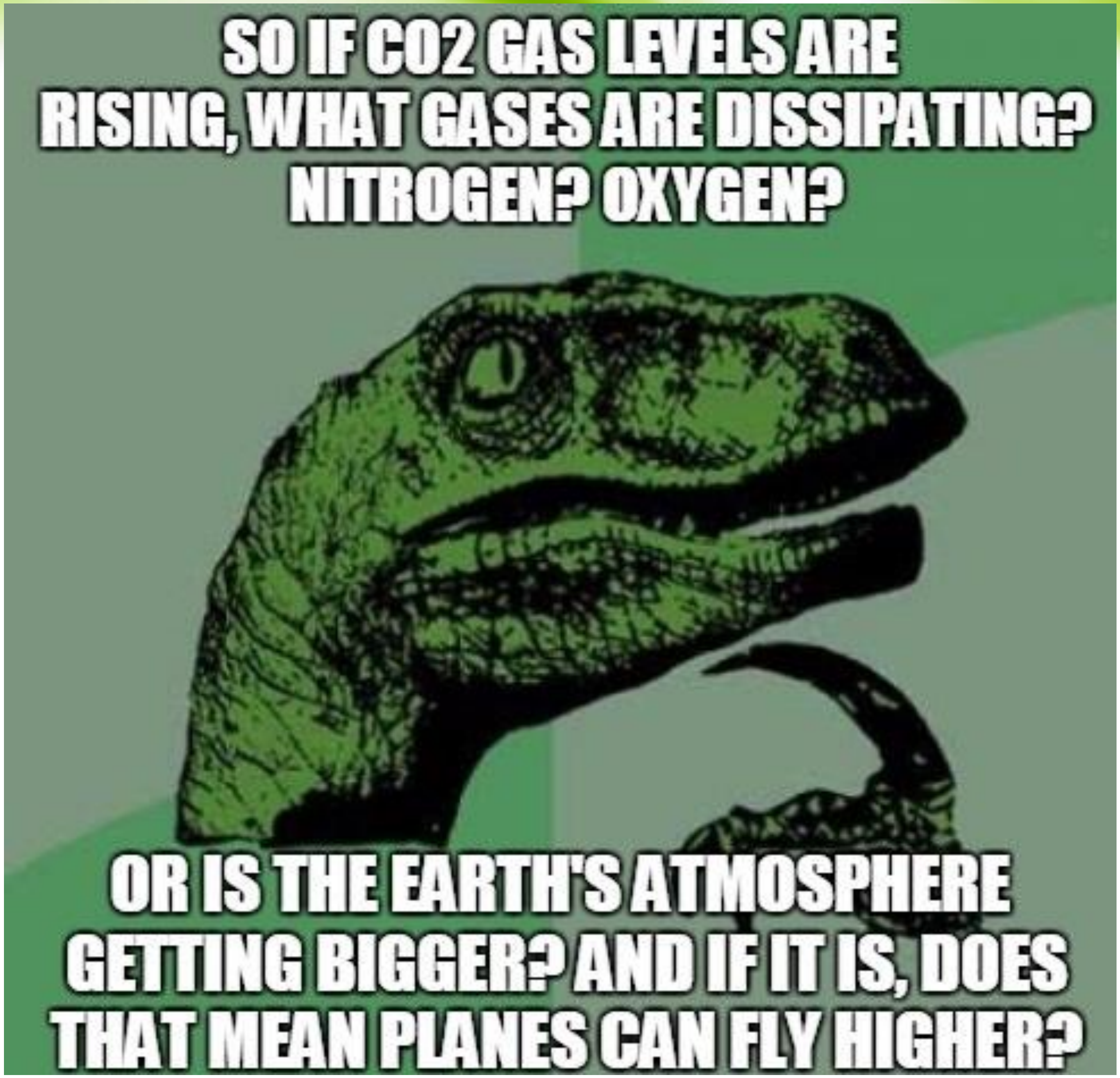

CO2 in volcano gases
Arc volcano
Sediment
CH4 and CO2 in forearc fluids
C in organic matter and carbonate minerals
Oceanic lithospere
Accretionary prism
Crust
C in crustal fluids
Lithospheric mantle
C in magmas
Mantle flow
C in slab fluids
Mantle flow
Subducting slab
Arc magma source
C in slab fluids
Asthenospheric mantle
Asthenospheric mantle
C mostly in carbonate minerals carried to deeper mantl
Manning, 2014

# Subduction




(Diagram adapted from U.S. DOE, Biological and Environmental Research Information System.)

# Thank your for your attention



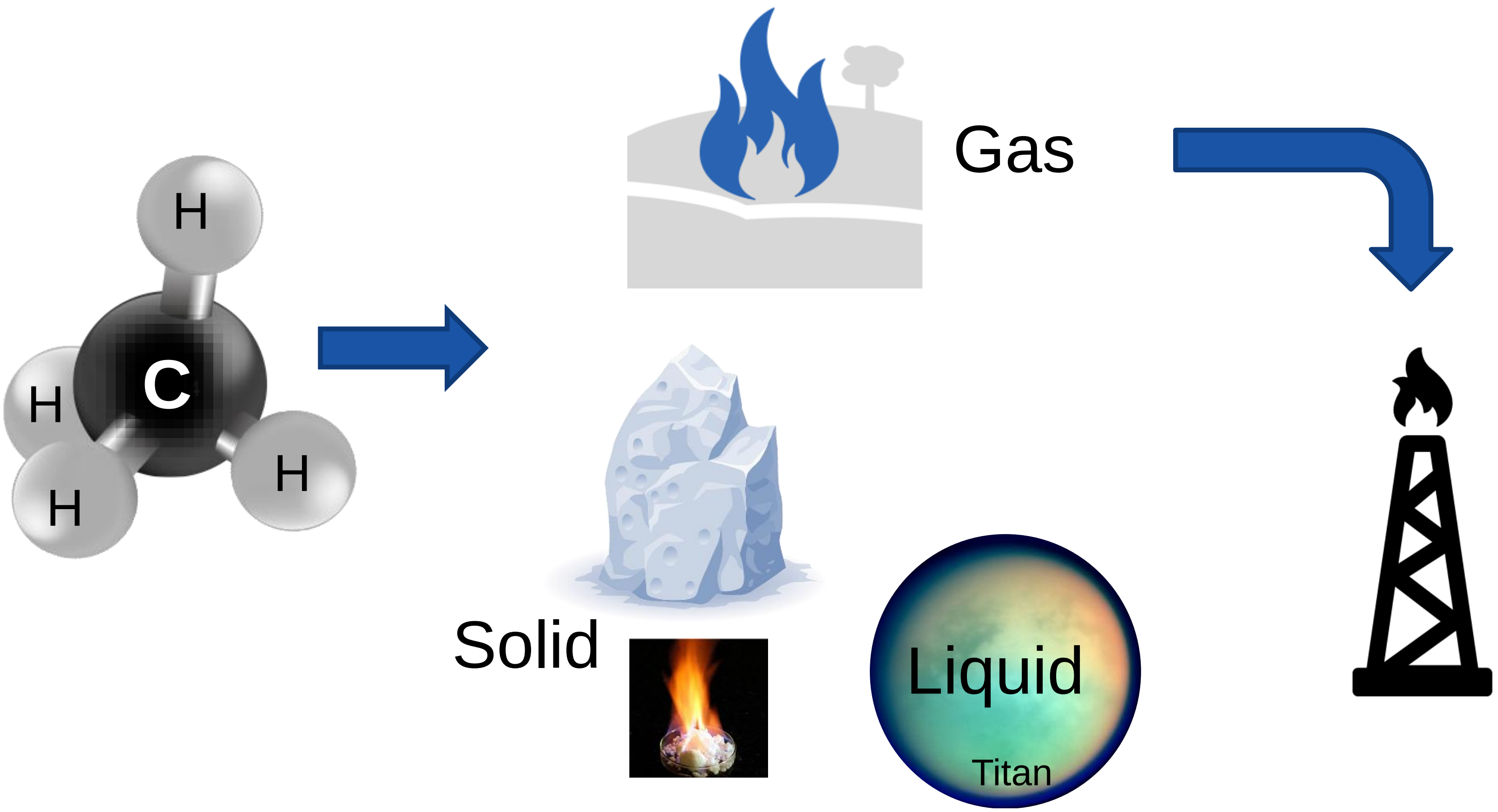
KTH ROYAL INSTITUTE
OF TECHNOLOGY

# Deep methane in the global methane budget

Elena Mukhina

Lecture | Stockholm, Sweden | December 1-4th 2017

# Methane

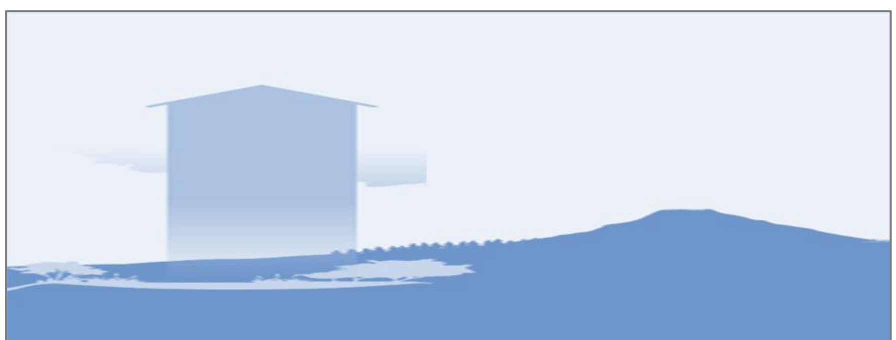


# Methane emission to the atmosphere

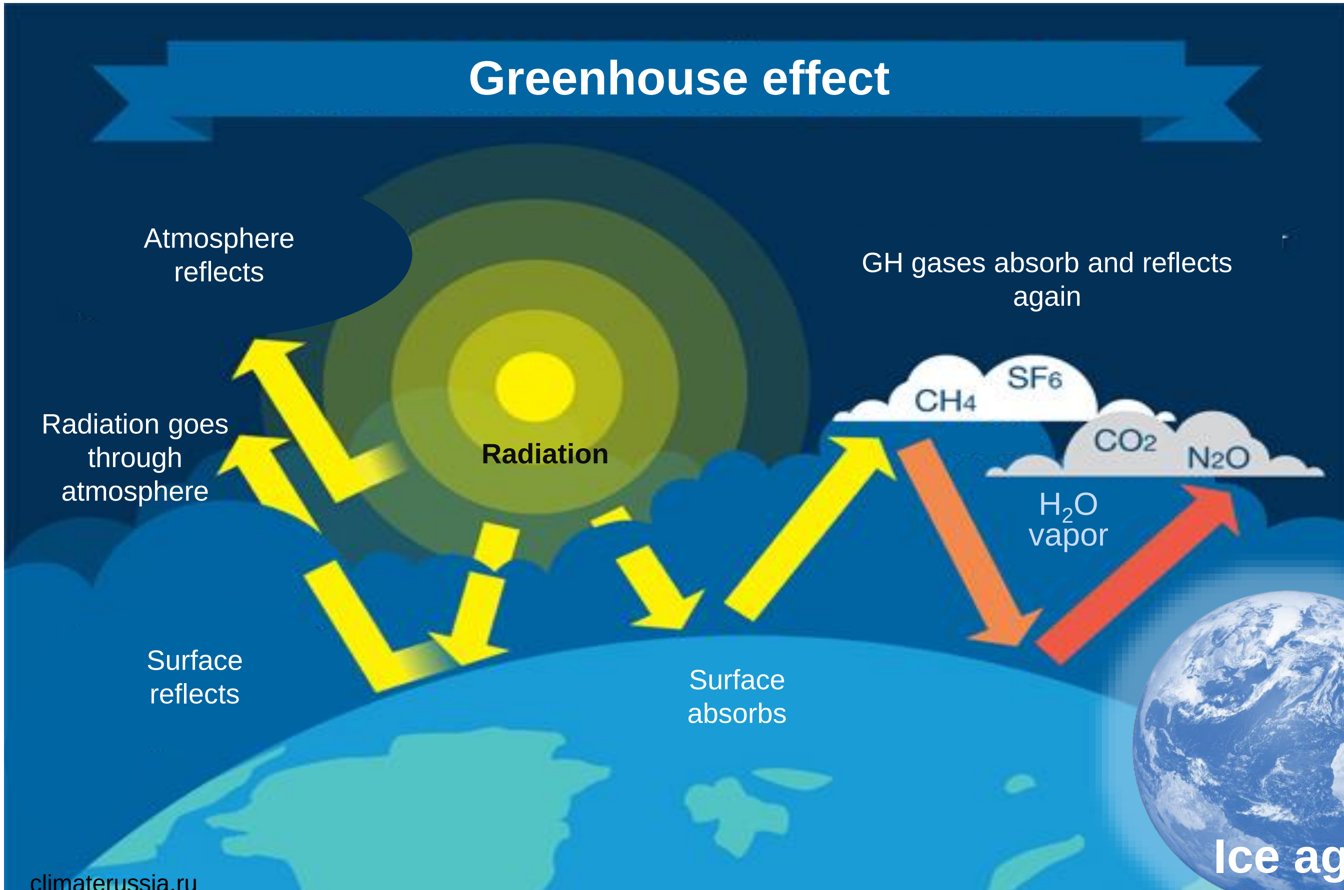
Methane accumulation in the atmosphere

Accumulating Heat

- Changing climate
- Green house effect
- Affecting physics and biogeochemistry of the Earth



# Greenhouse effect – natural process




(Earth, Now)
Contribution
to GHE

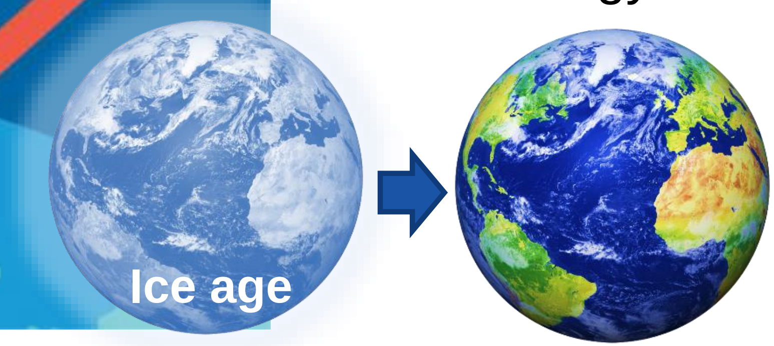
$H_2O$ vapor – up to 70 %

$CO_2$ – up to 26 %

$CH_4$ – up to 9 %

Radiation

Heat energy



# Methane and $CO_2$ in atmosphere

**Concentrations**

0.036% $CO_2$ = <u>200</u> * 0.00018% $CH_4$

**Amount in atmosphere (NOW)**

$CO_2$ <u>~3000</u> Gt ***vs.*** $CH_4$ <u>~5</u> Gt

Less than 1%!!

**Contribution to the climate change**

$CH_4$ = <u>30%</u> of $CO_2$

<u>5 Gt</u> $CH_4$ = <u>900 Gt</u> $CO_2$

(absorbs radiation)

How much heat the gas traps in the atmosphere

$CH_4$ = <u>860%</u> * $CO_2$

Rising concentration last 200 y

<u>150</u>% $CH_4$ ***vs.*** <u>40</u>% $CO_2$

# Increasing of methane in atmosphere

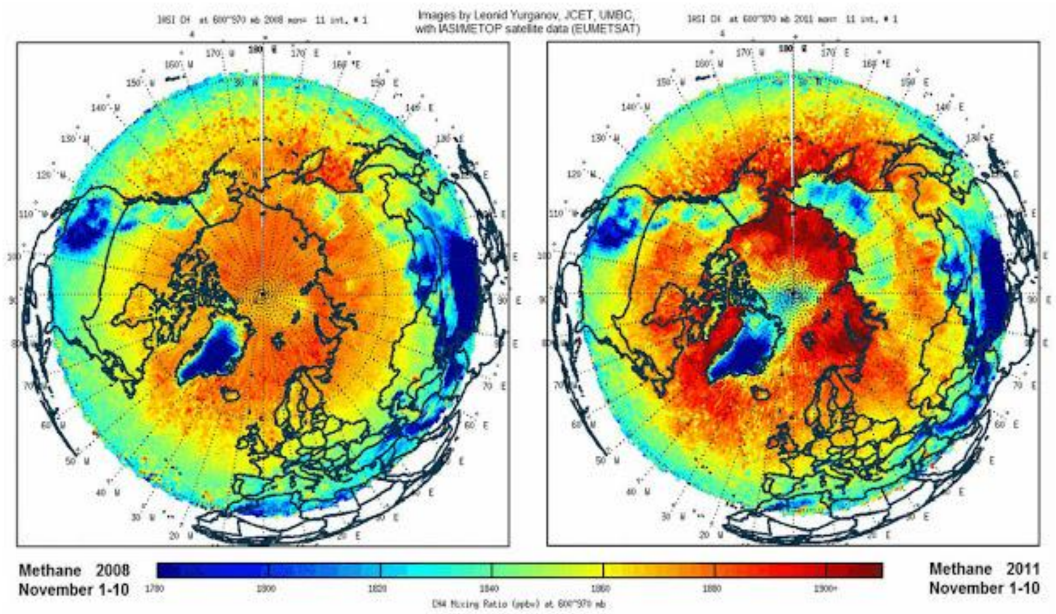



Figure 2. AIRS atmospheric methane concentration data showing an anomalous buildup of methane over the Arctic region from November 2008 to November 2011 Diagram from Yurganov 2012 in Carana 2012.

**Current concentration of $CH_4$**
**5 Gt ~ 5000 Tg**

***Emissions***
**~ 720 Tg per year**

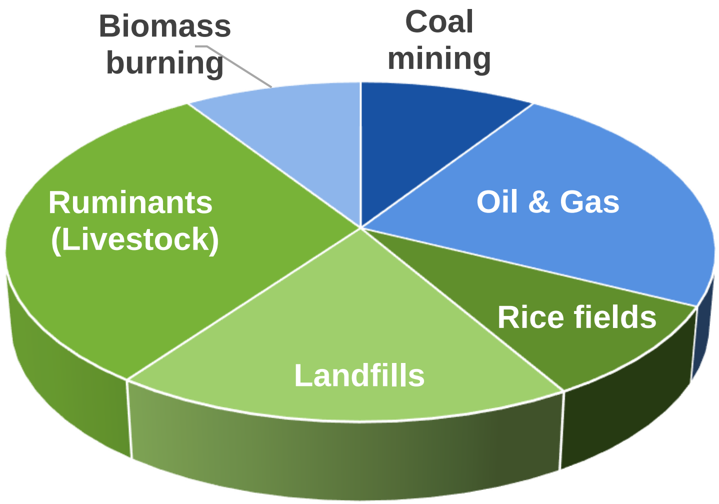
***Removal***
**~ 710 Tg per year**

***Imbalance***
**~ 10 Tg per year**

# Where this methane emits from?

# Anthropogenic methane emissions

***Total***
**~ 720 Tg per year**



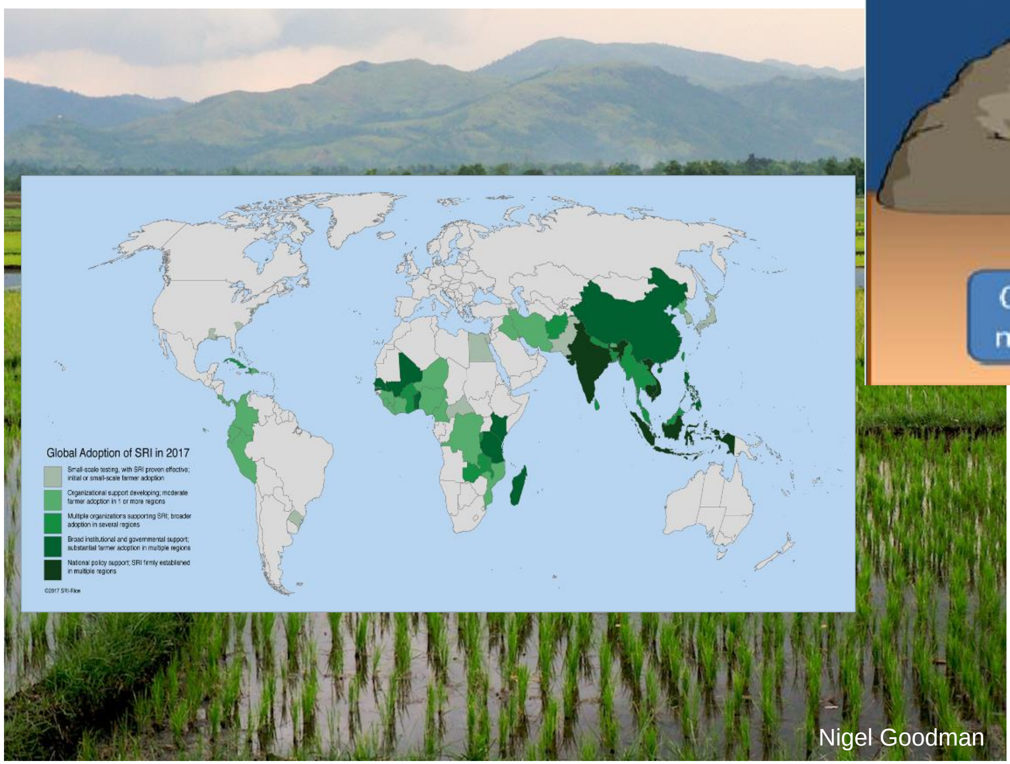

**335 Tg per year**

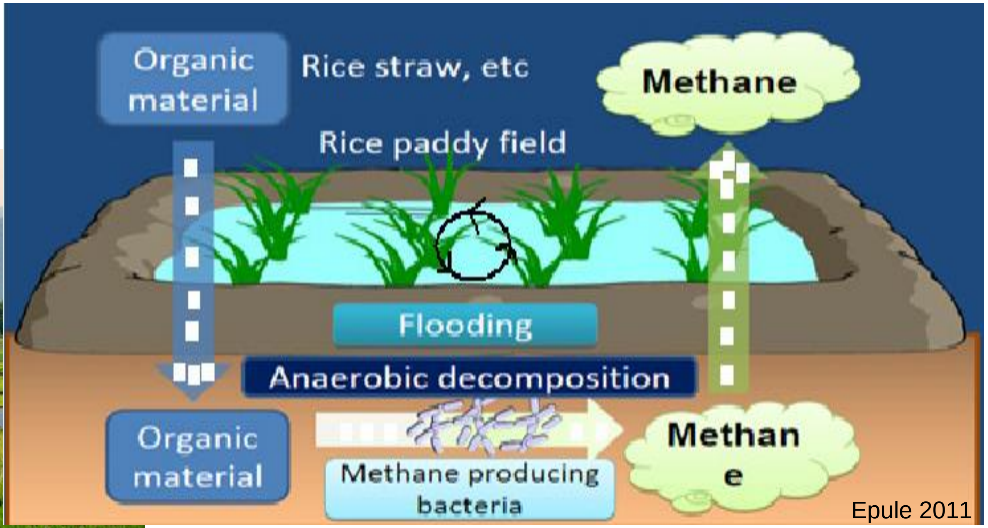
| Source | Tg per year |
|---|---|
| Livestock | ~100 |
| Landfills | ~60 |
| Rice fields | ~30 |
| Coal mining | ~40 |
| Gas, oil, and industry | ~75 |
| Biomass burning | ~18 |
| Biofuel burning | ~12 |
| Total anthropogenic | ~335 |

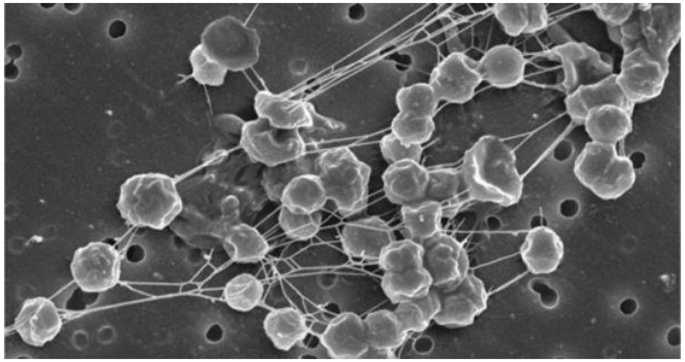

**Obvious?**

Suanois 2016

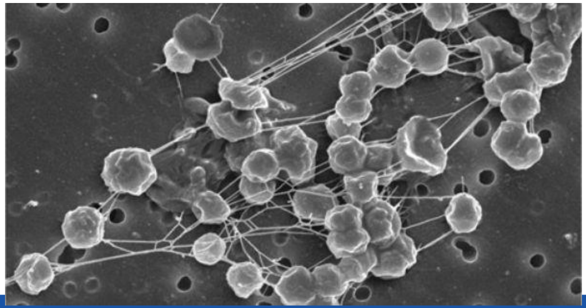
# Methane emissions from rice fields

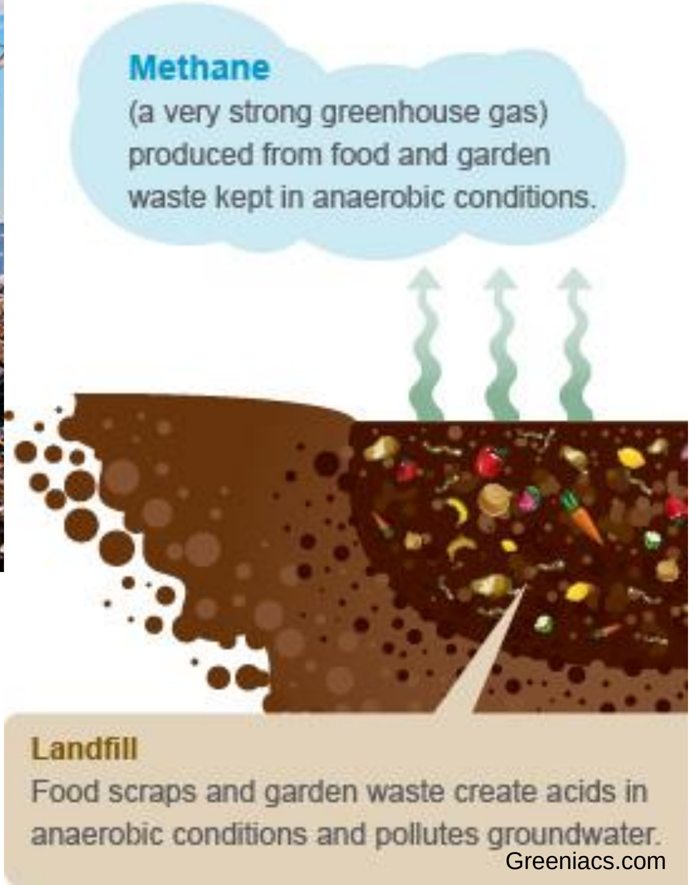


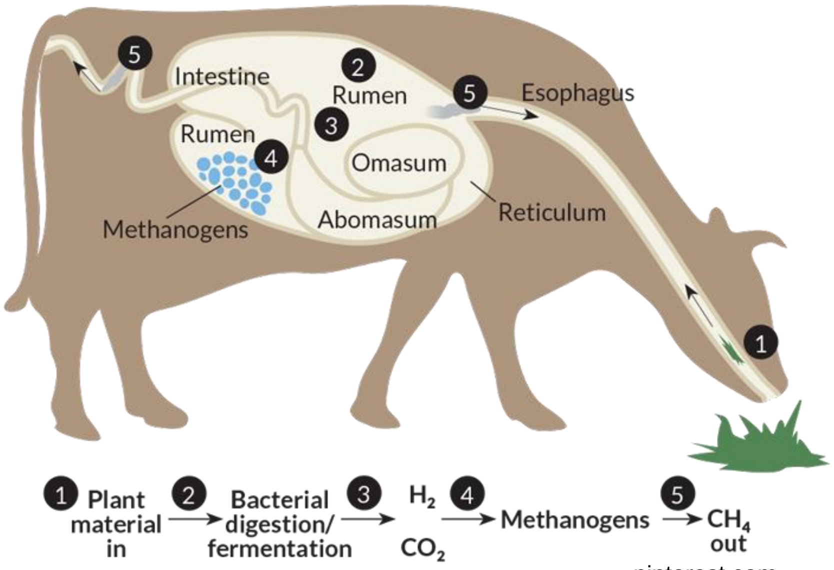
# Methane from landfills



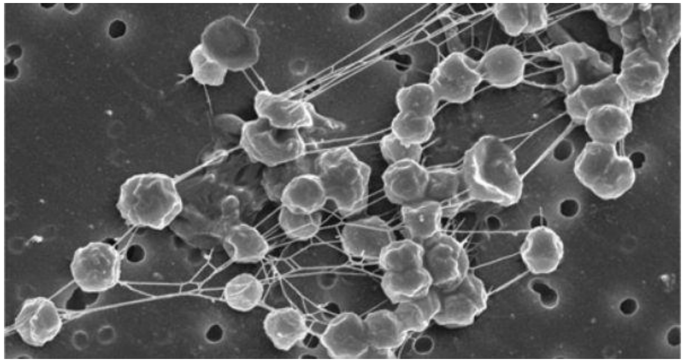


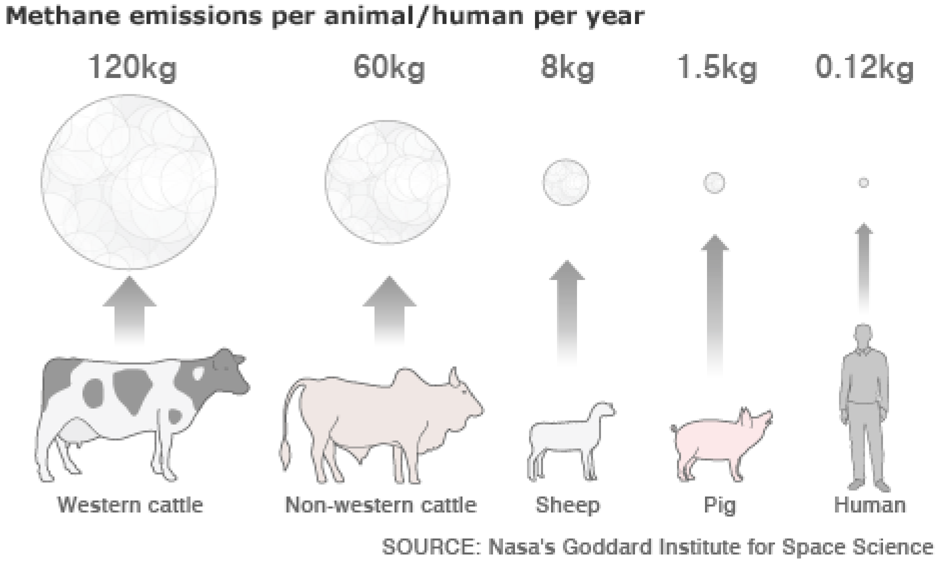

Greeniacs.com

# Methane from livestock




pinterest.com






**~ 100 Tg per year**

**Compare to Oil & Gas!**
**~ 75 Tg per year**

***Total***
**~ 720 Tg per year**

# Natural methane emission

**~ 400 Tg per year**

# Global carbon cycle

*Total*
~ 720 Tg per year

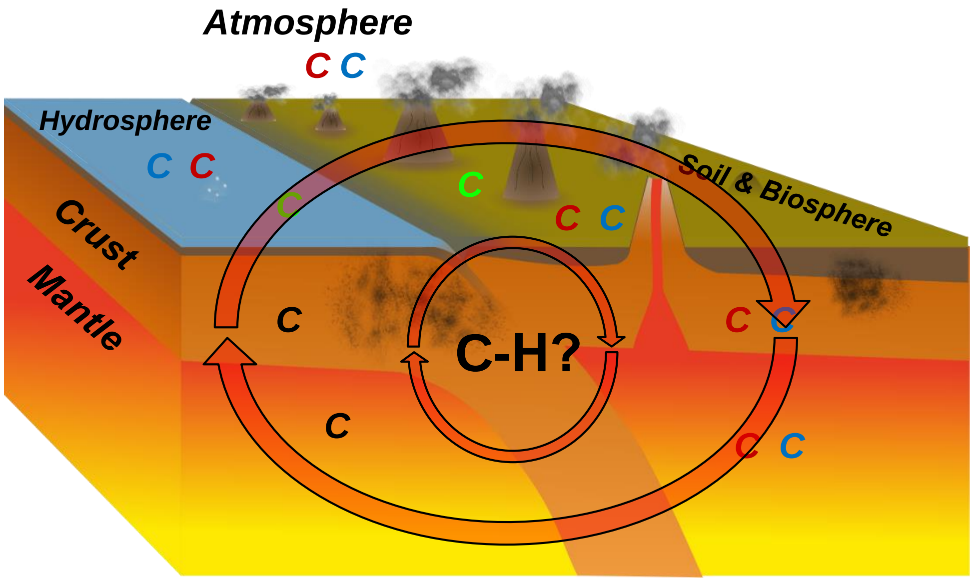
What is carbon on Earth?

**Native *C* minerals – graphite, diamonds, coal**

**Oxidized *C* – $CO_2$, *CO*, carbonates like $CaCO_3$**

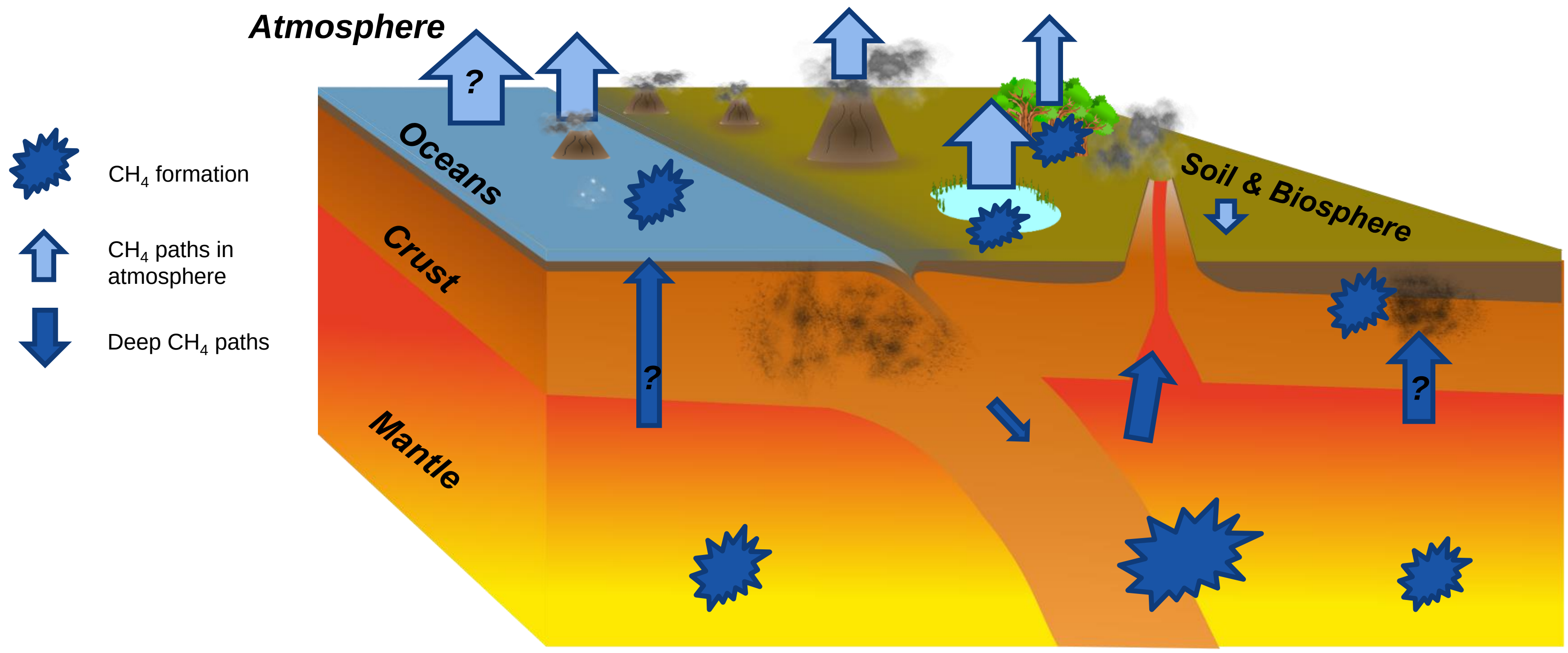
**Reduced *C* – $CH_4$ (methane) and other hydrocarbons**

**Complex organics – living organisms**



# Methane as a part of the global carbon cycle

***Total***
**~ 720 Tg per year**



# Methane removal from atmosphere and soil

photo-dissociation

**Lifetime** ~12 years

$O_3 + h\nu \rightarrow O\cdot + O_2$

$O\cdot + H_2O \rightarrow \cdot OH + \boldsymbol{\cdot OH}$

***Hydroxyl radical***

$\mathbf{CH_4 + \cdot \mathit{OH} \rightarrow \cdot CH_3 + H_2O}$

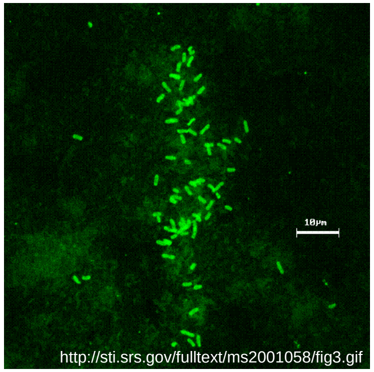
$\cdot CH_3 + O_2 \rightarrow CH_3O_2\cdot$

$CO_2$

**~ 650 Tg per year**

Methanotrophic bacteria in soil

- $CH_4 \rightsquigarrow CO_2$




**~ 50 Tg per year**

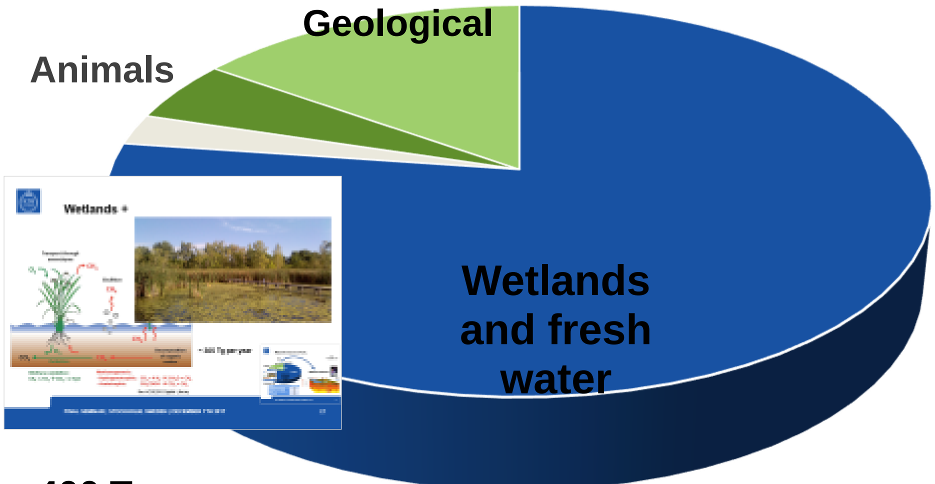
$\uparrow CH_4$ in the atmosphere ⇨ $\downarrow \cdot \mathit{OH}$ ✚ Longer $CH_4$ life

12 years ?

# Natural sources of $CH_4$

*Total*
**~ 720 Tg per year**

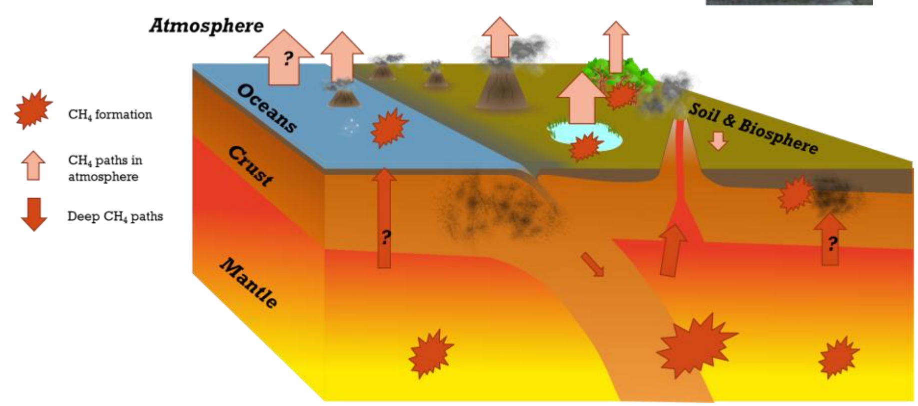
**?**



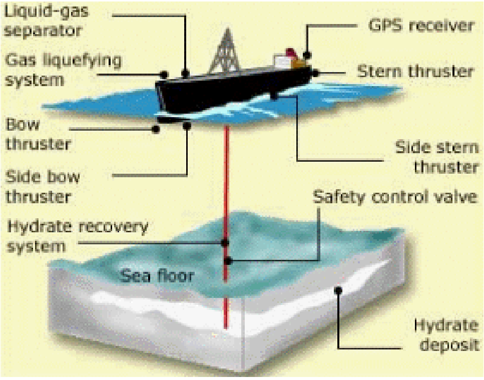

**~ 400 Tg per year**

| Source | Tg per year |
|---|---|
| Wetlands and fresh waters | ~305 |
| Geological, incl. hydrates | ~55 |
| Wild animals, incl. termites | ~20 |
| Other | ~15 |
| Total natural | ~400 |

## Methane hydrates



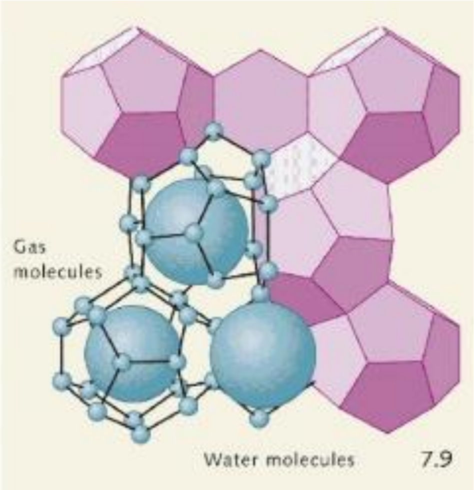
# Methane hydrates



BBC News

Clathrates

Ice



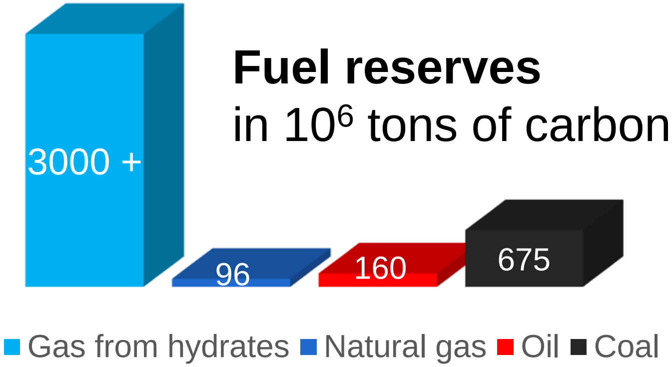


World Ocean Review

500 – 11000 Gt
of methane in hydrates?

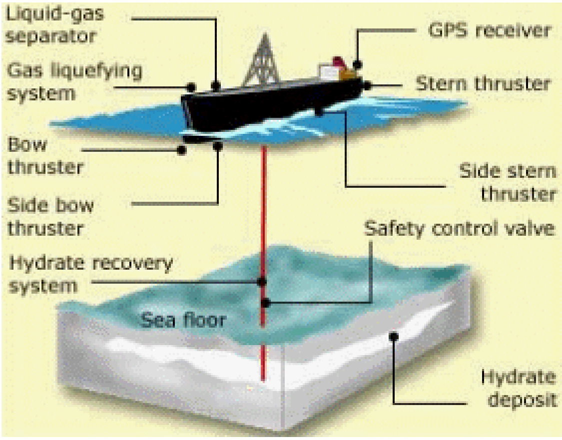
1 m$^3$ of hydrates contains
~160 m$^3$ of methane!


Geomar



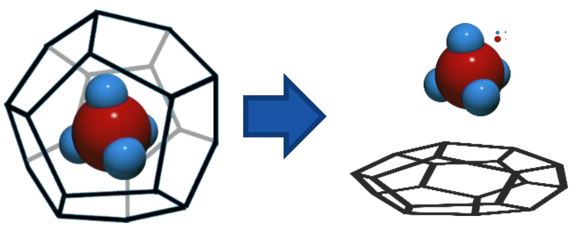
Archer & Buffett, 2007

# Methane as a fuel

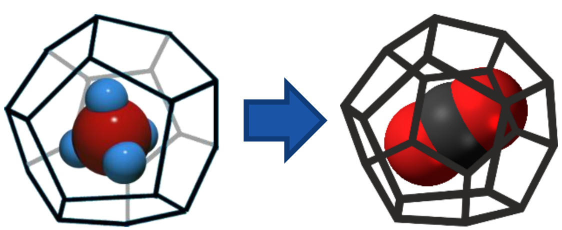



Destructive
Unsafe for environment

**Methane is a part of Nature same as wind or water**



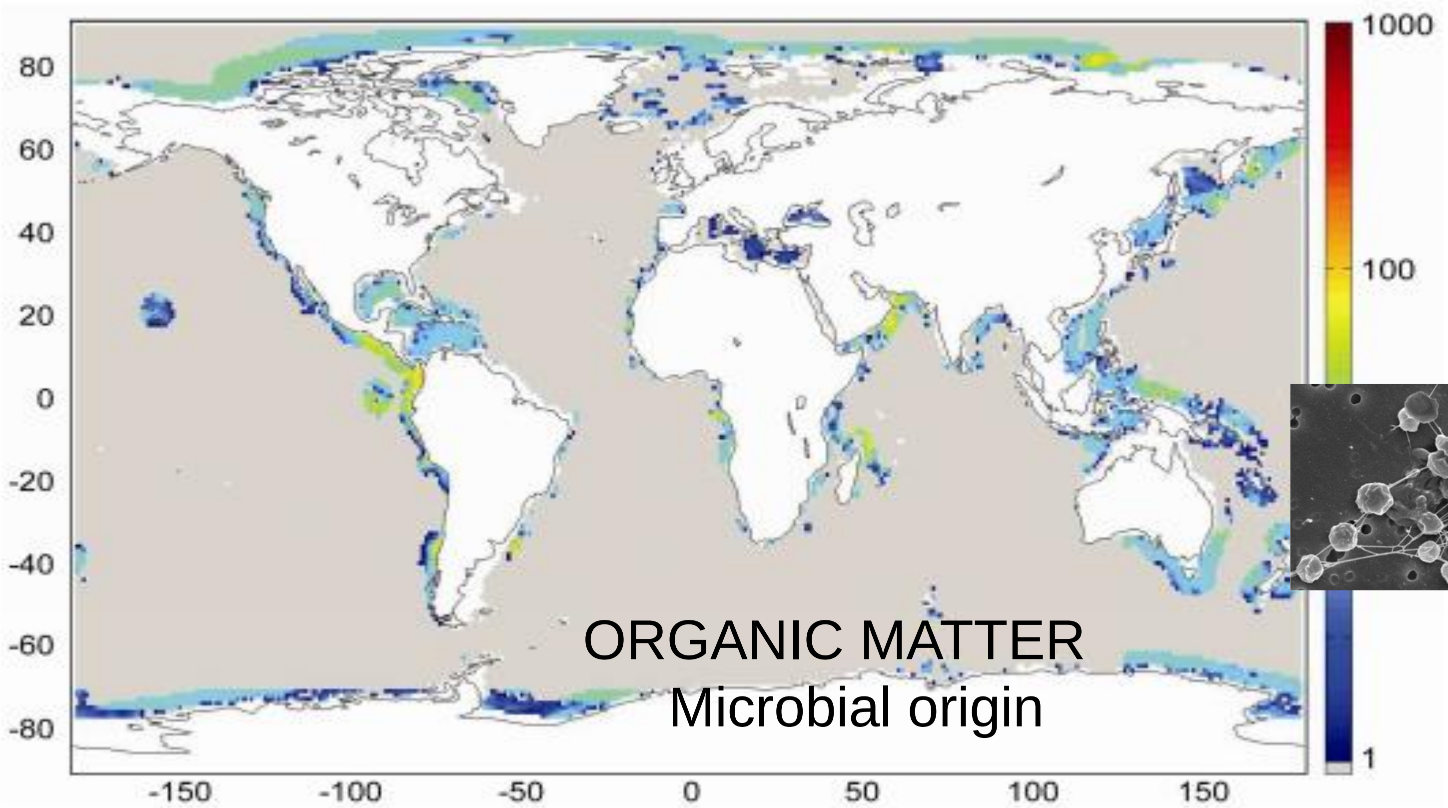
Depressurization



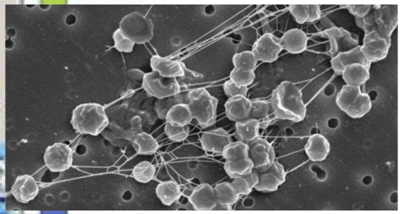
Methane substitution

Non-destructive
Environmental friendly

# Methane hydrates on Earth




Methanogenic bacteria

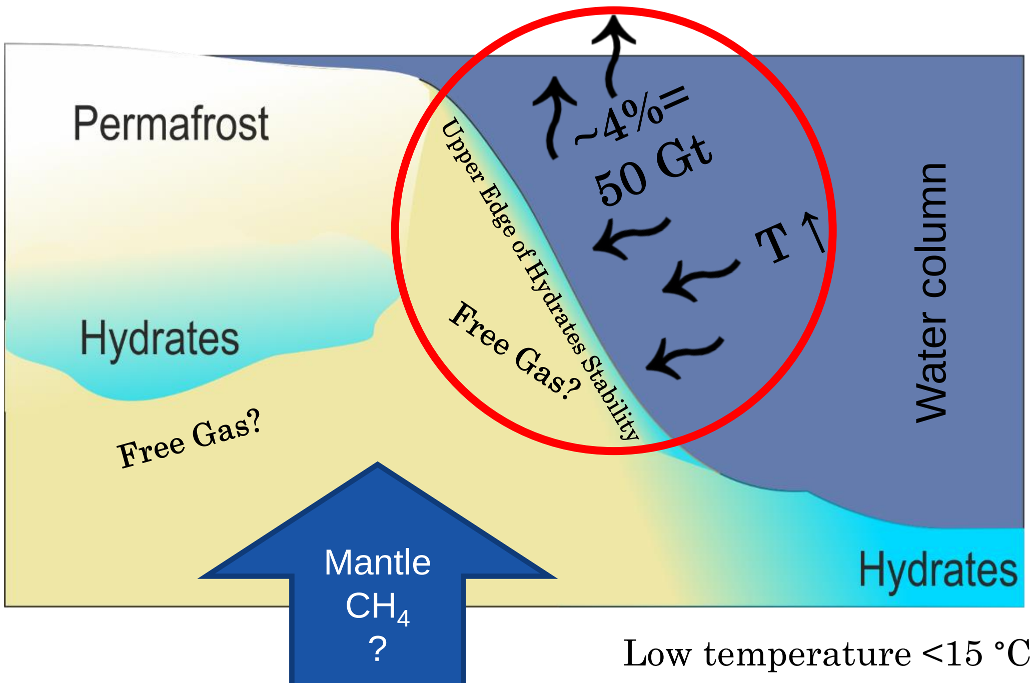


???

Wallmann 2012

# Methane hydrates on Earth

ESAS = 1700 Gt of $CH_4$ in hydrates





Low temperature <15 °C
Pressure 3-12 MPa

**Current $CH_4$ concentration in the Earth's atmosphere - 5 Gt**
Currently increases in **0.01 Gt** per year

# Mantle formation of methane

***inorganic***

Source of Carbon [C]

+

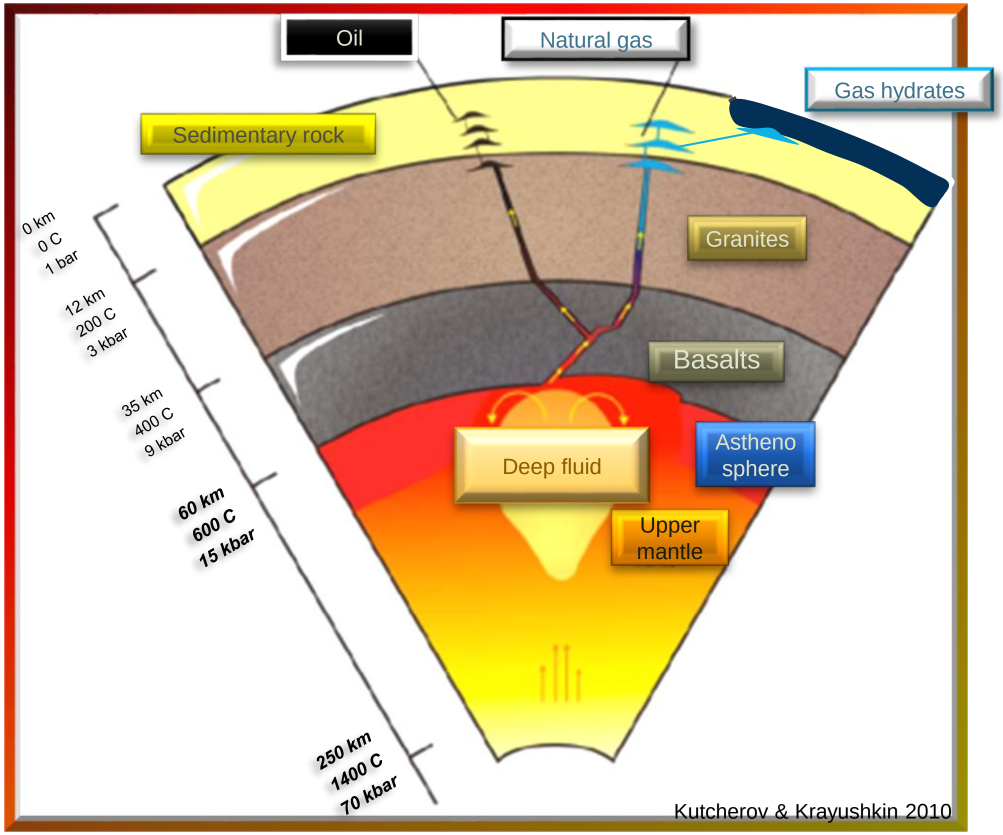
Source of Hydrogen [H]

{CH} fluid

Migration up

Accumulation

***Deep abiogenic genesis of hydrocarbons***




Kutcherov & Krayushkin 2010

# Experiments

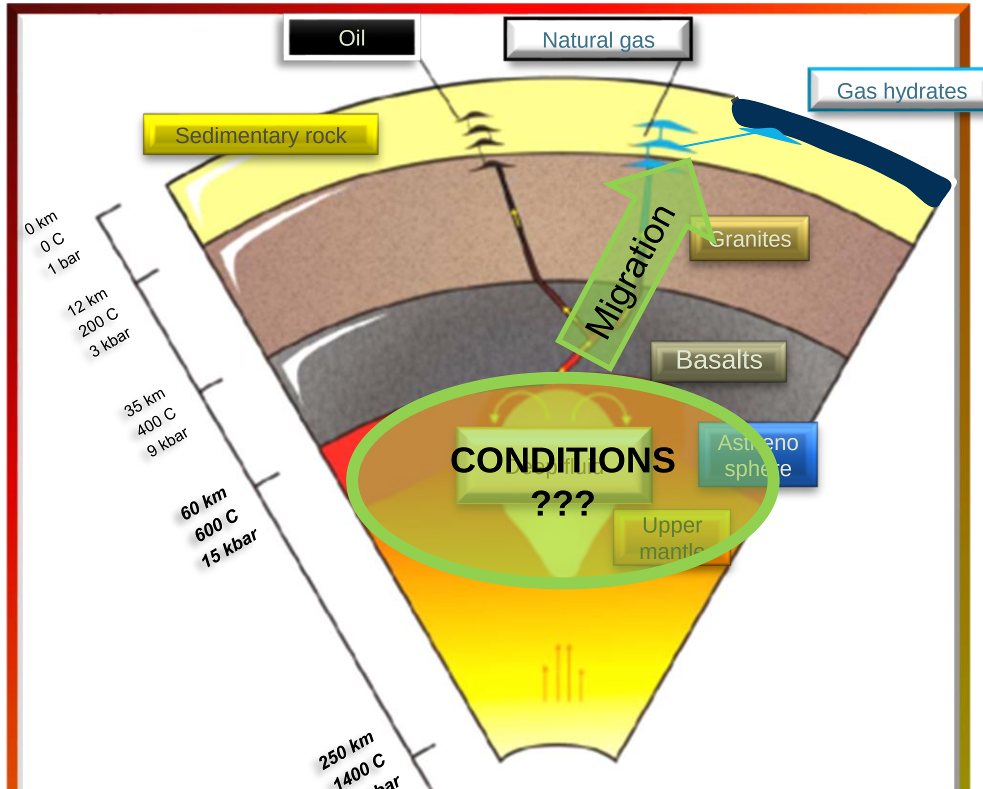
Main goal:

The relationship between mantle methane and formation of methane hydrates.

Tasks:

1. **pT** conditions of deep $CH_4$ formation
2. **Redox** conditions of deep $CH_4$ formation
3. Migration paths of $CH_4$ and hydrate formation

DEPTH



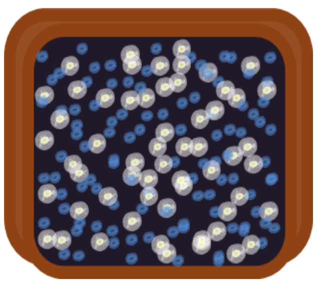

Kutcherov & Krayushkin 2010

# Experiments

**Experiments (High pressure, high temperature)**

Large reactive volume device

**Metallic sample container**



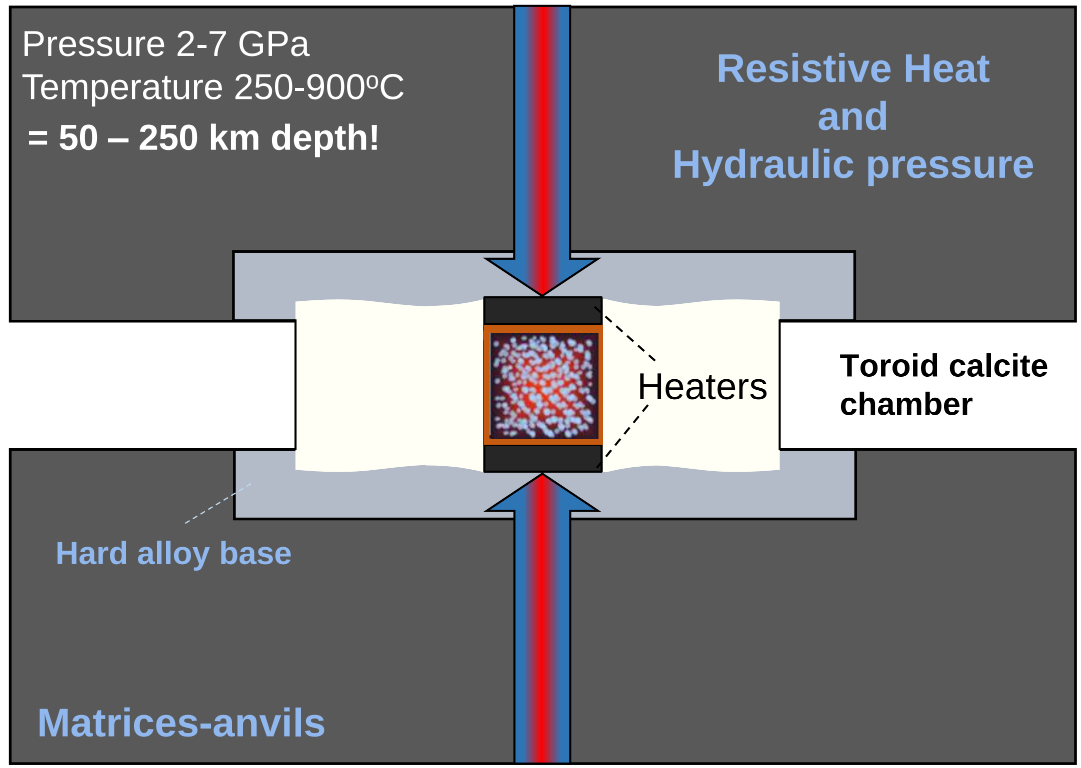
0,3 $cm^3$

*Oxygen buffer*

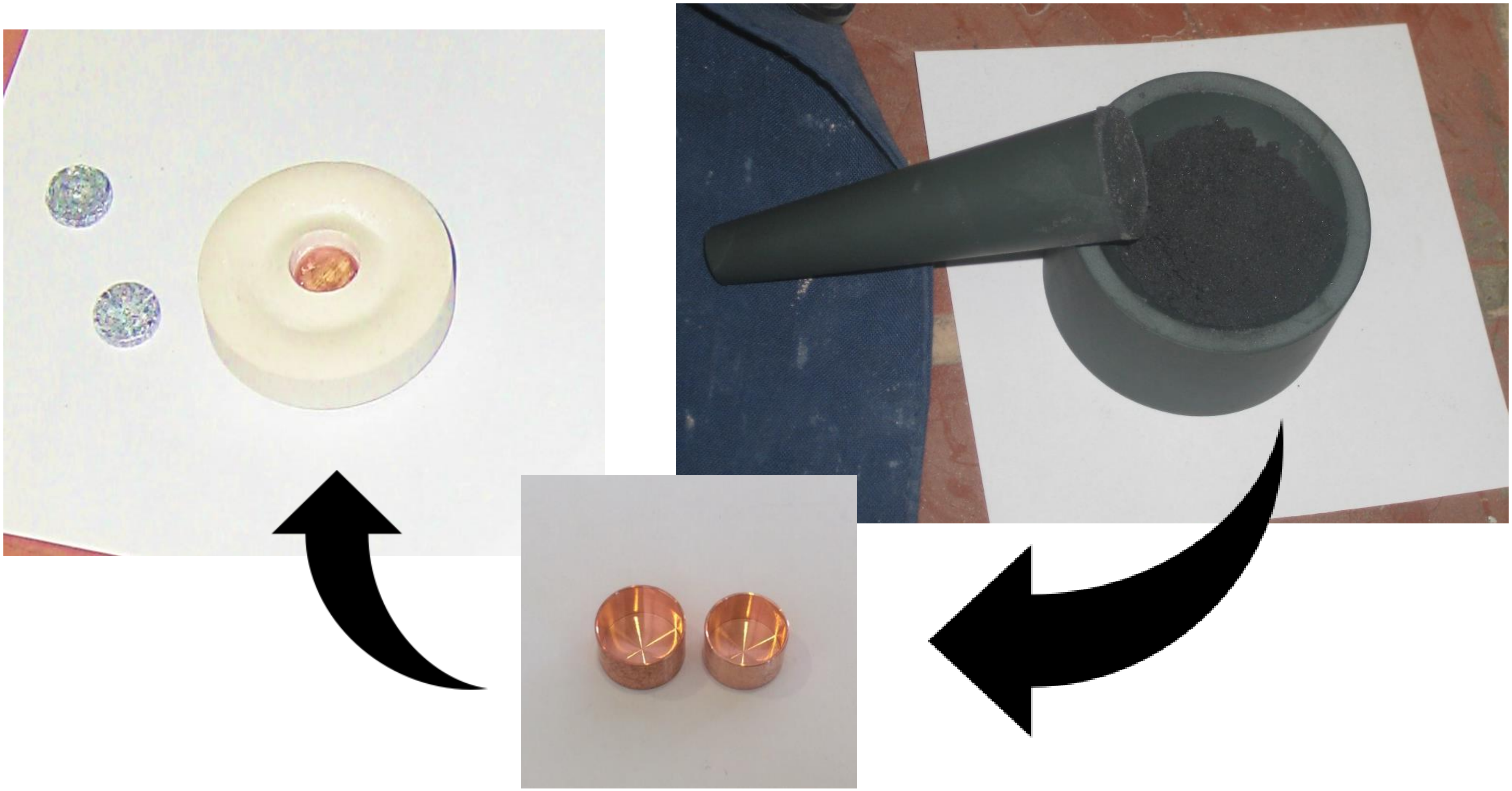
*$H_2O$* H – source

*$CaCO_3$* C – source

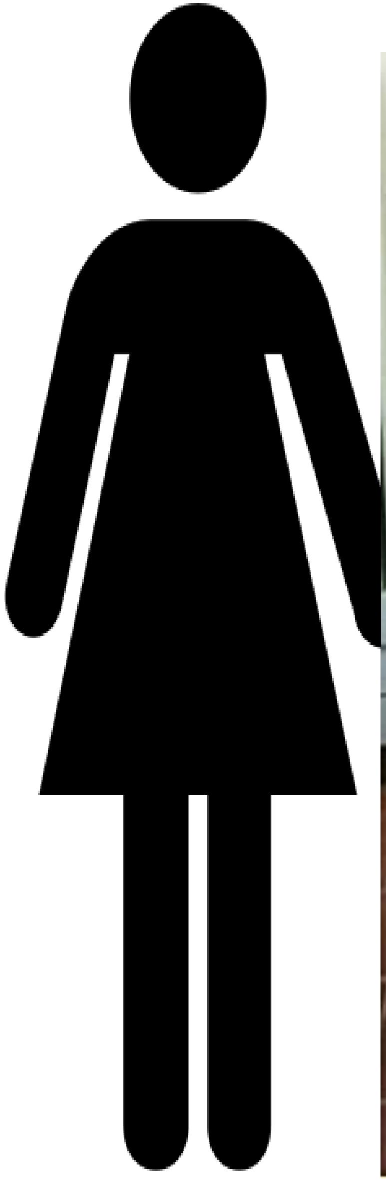
Inorganic!

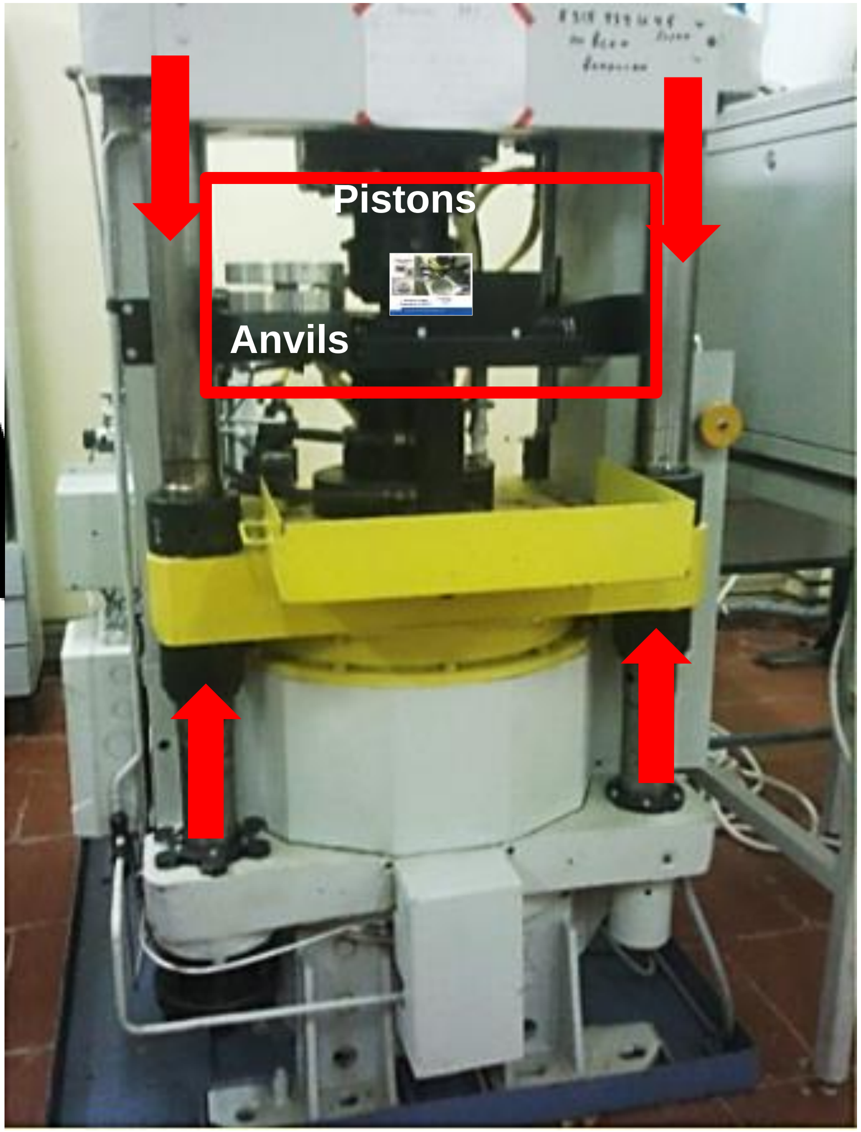


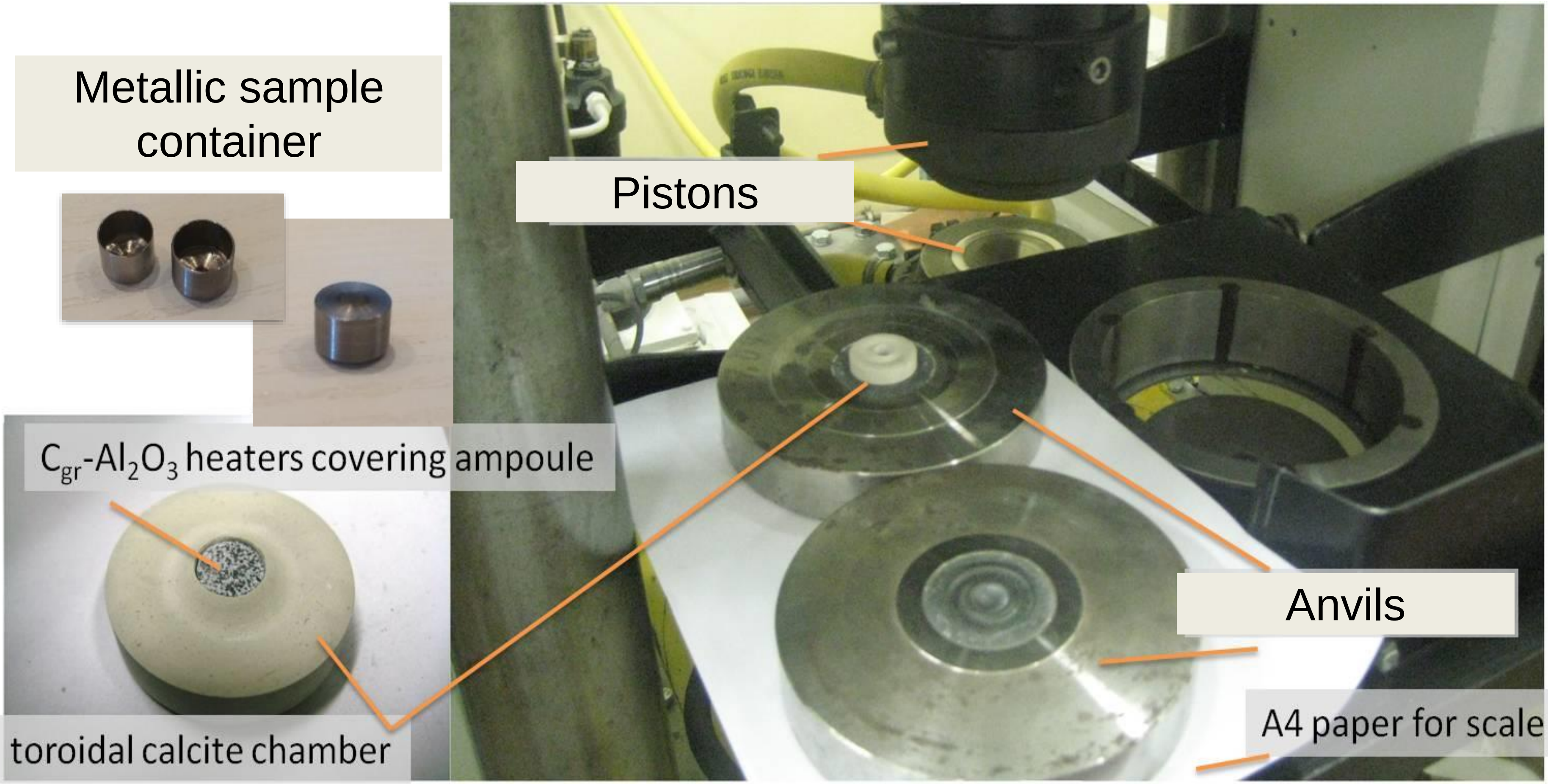
# Sample preparation



Large reactive volume device

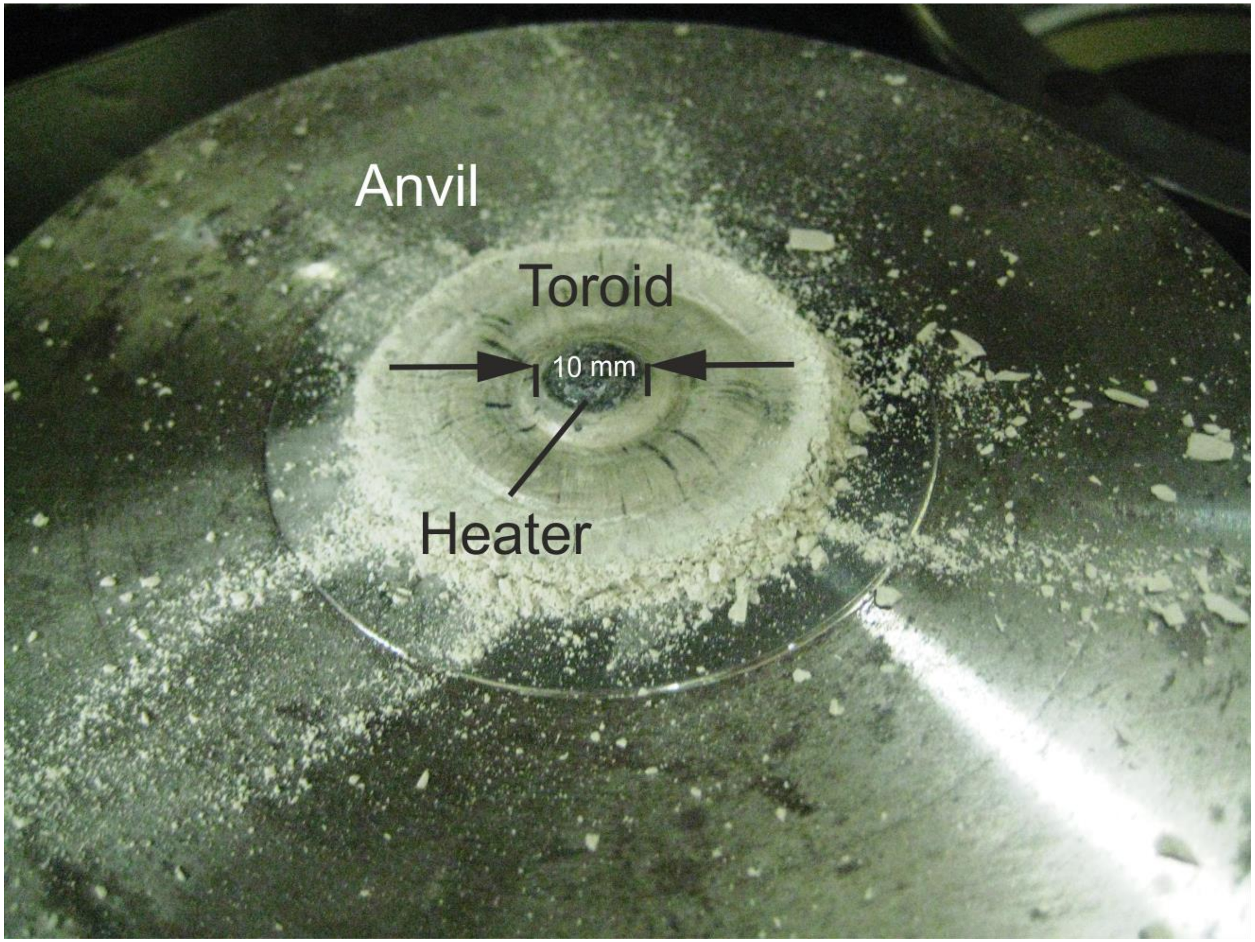







Duration of experiment: 5 sec to 48 hours

# Chamber after the experiment

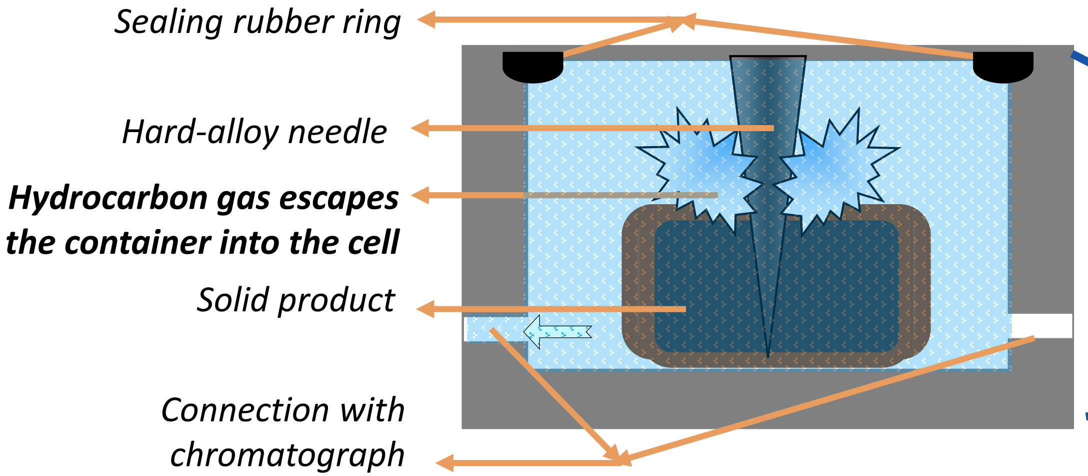


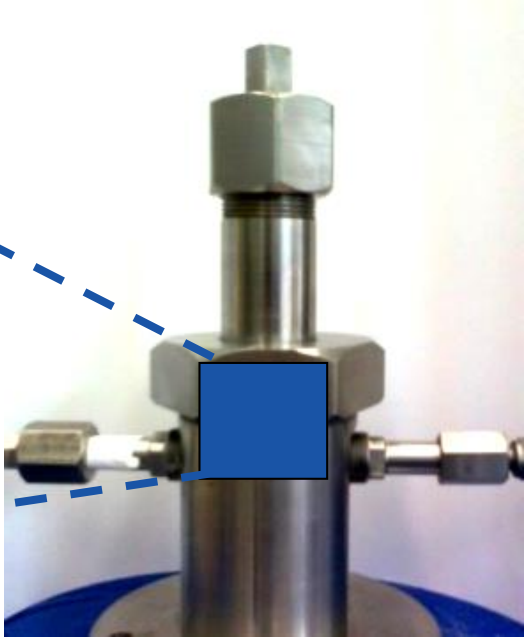
# Gas product analysis

**Identification of hydrocarbons**

Gas-extracting cell and gas chromatography

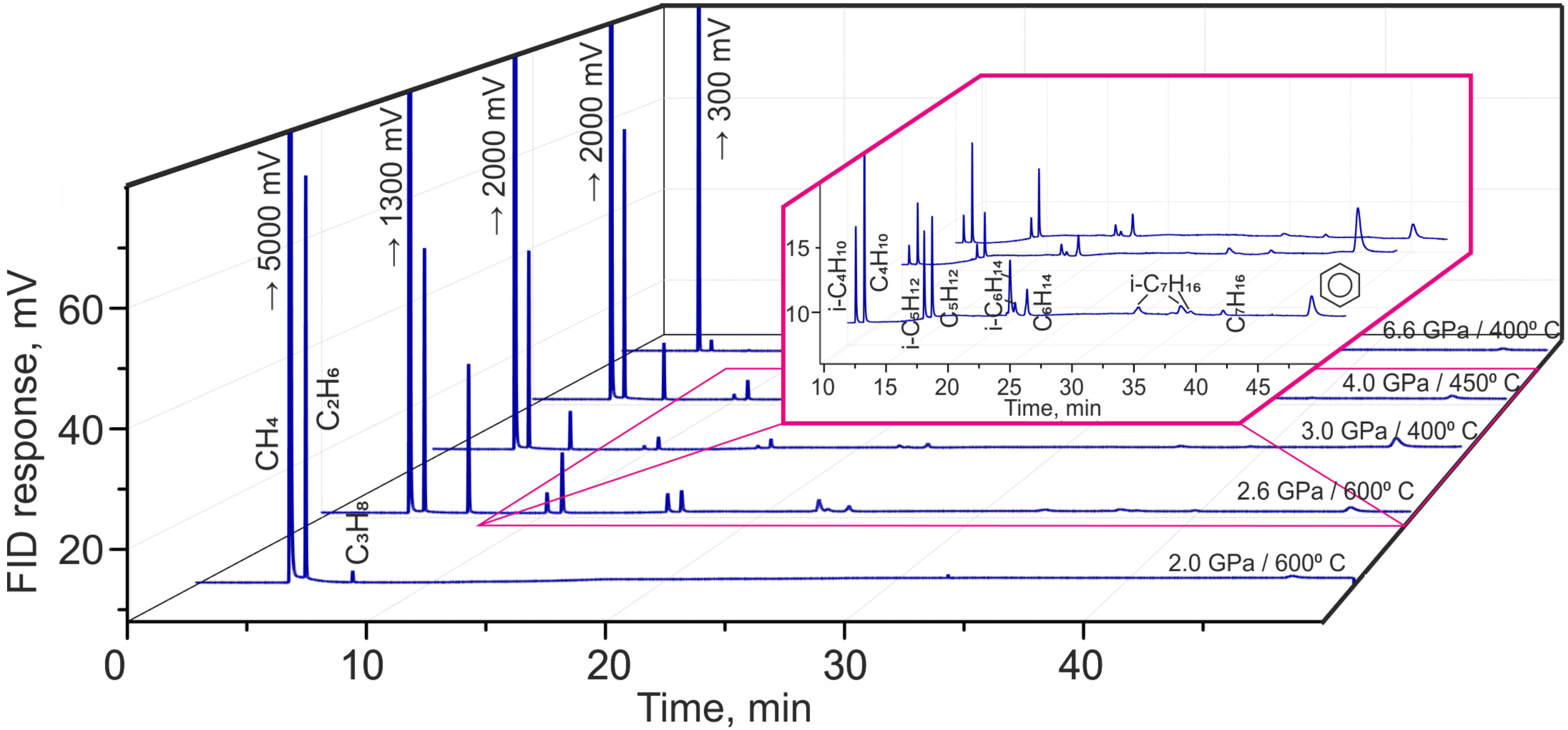
- Sealing
- Separation of individual hydrocarbons
- Quantitative analysis



**Gas-extracting cell**

# Chromatograms. Identification of hydrocarbons



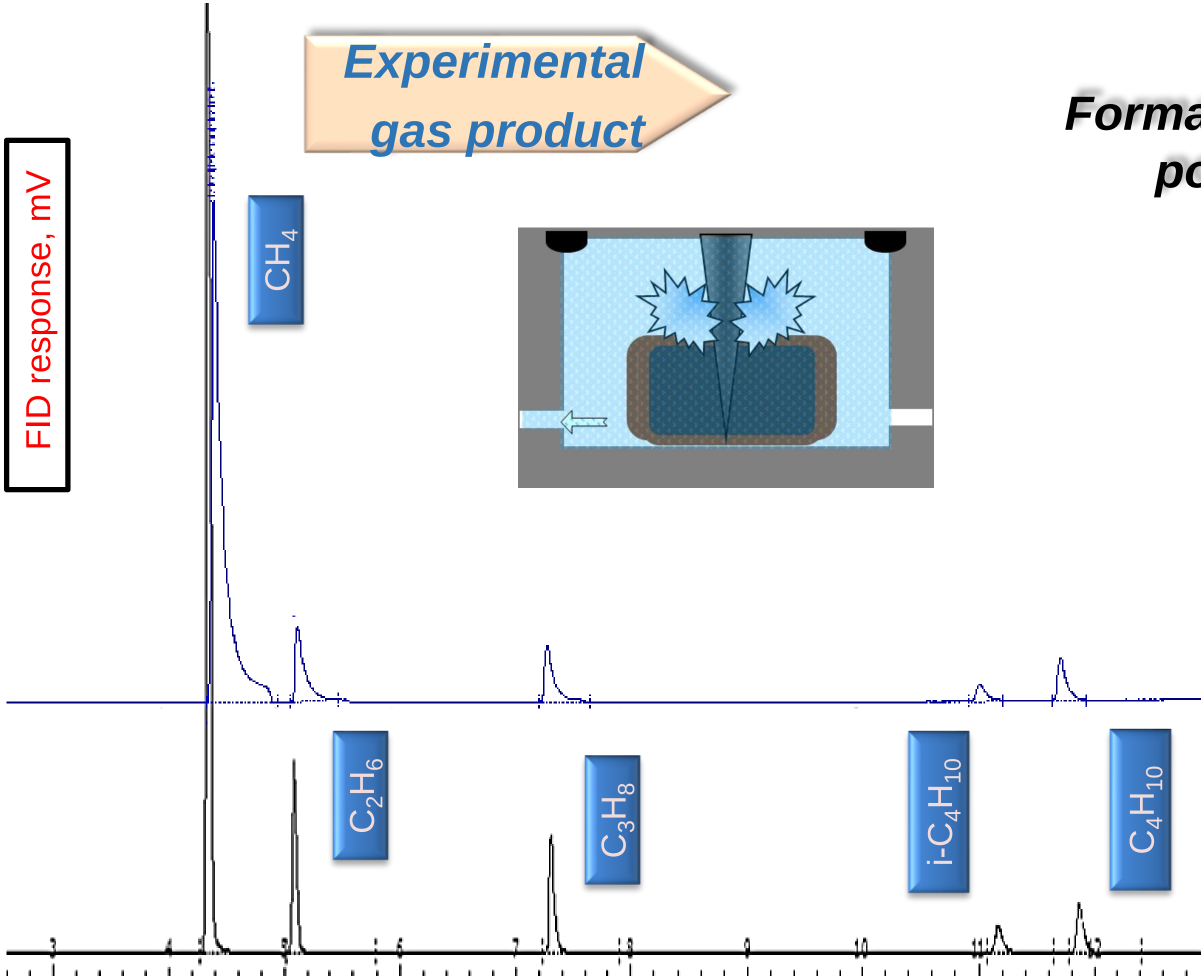

*From* ***$CaCO_3$ + $H_2O$*** *interaction*

# Large amount of hydrocarbon gas

**Bubbles after container gas analysis. Container is opened.**

**Exploded container**

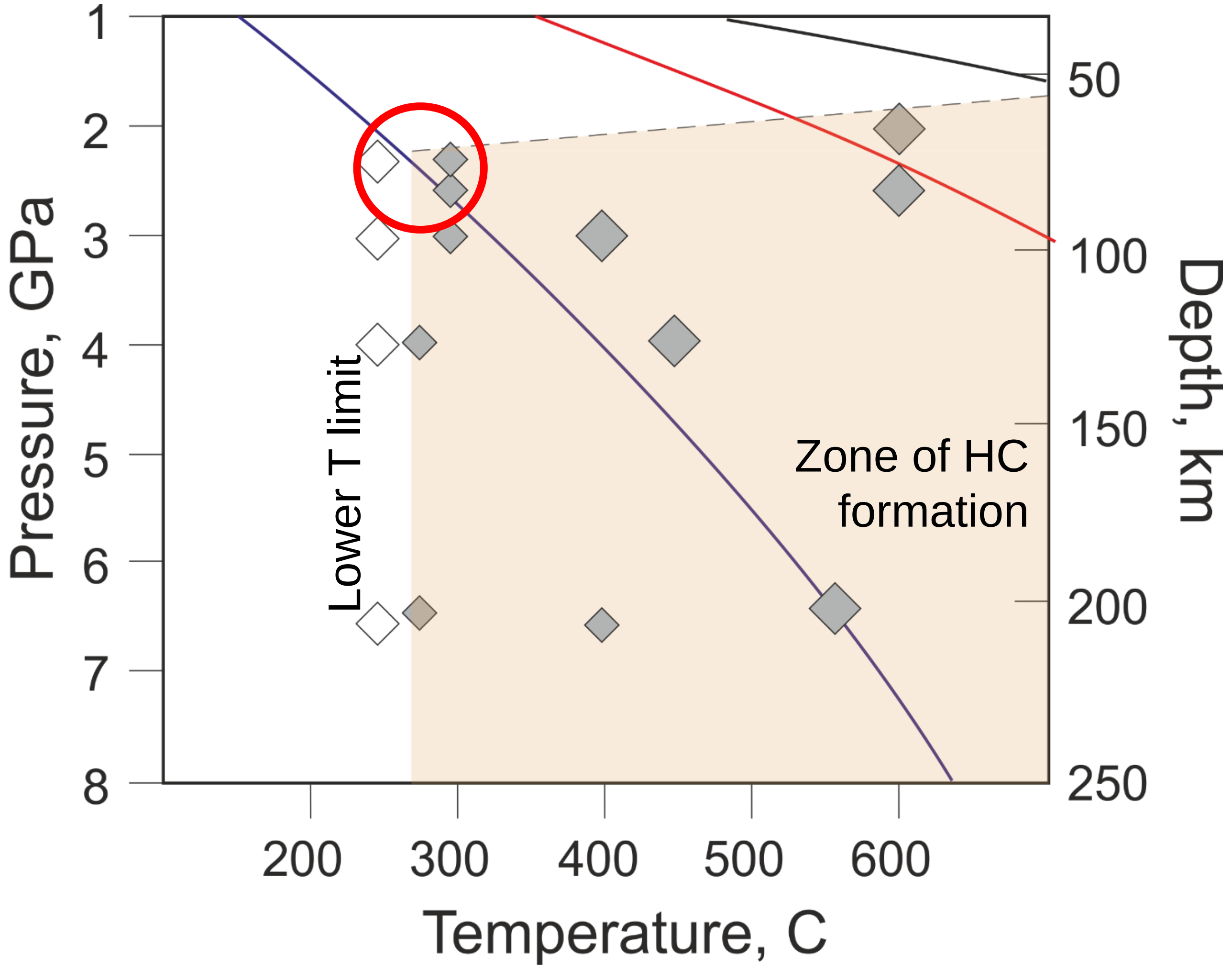
# Experimental gas product vs. Natural gas



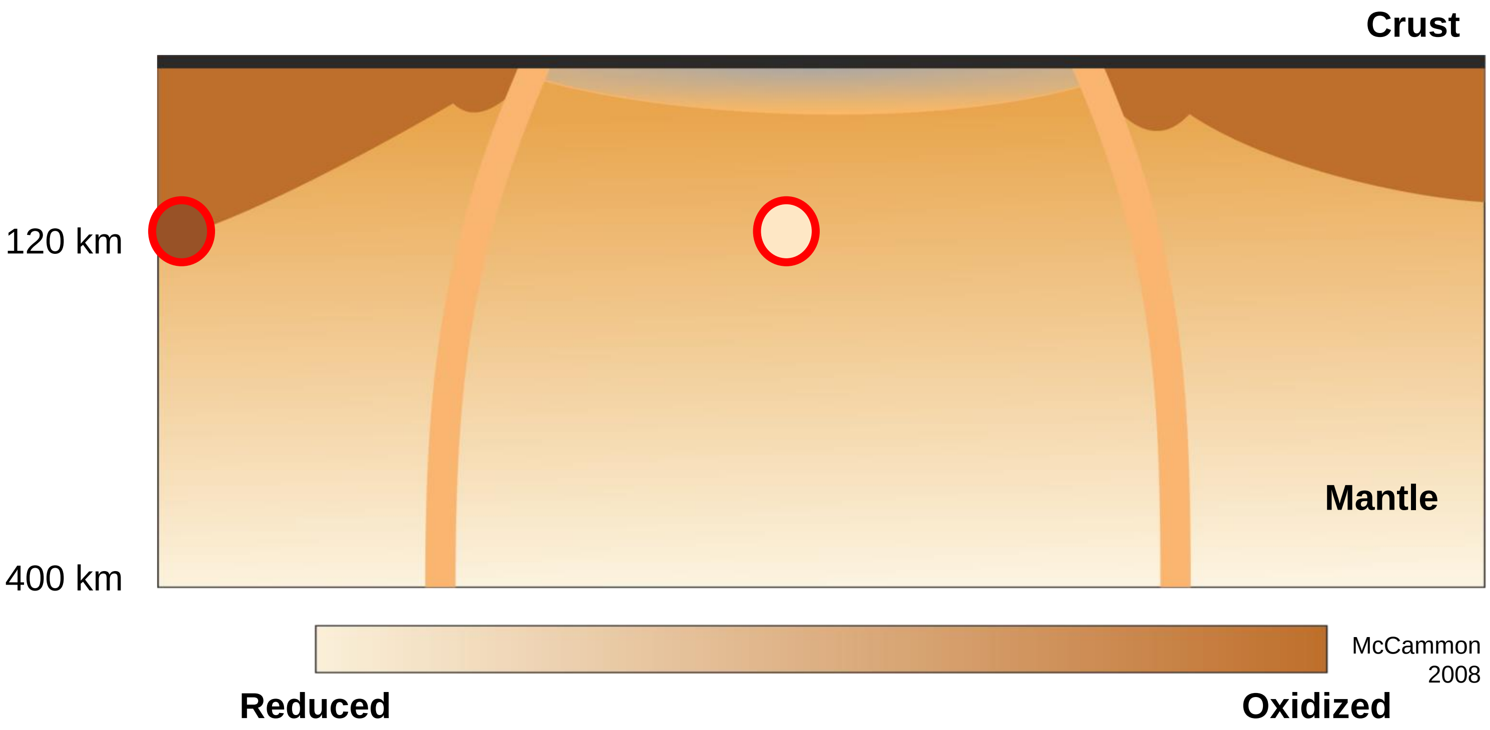

***Formation of natural gas is possible in mantle!***

# Experimental results 1. Depth limit

| Exp | P, GPa | T, ºC |
|---|---|---|
| **1.1** | 2.0 | 600 |
| **1.2** | 2.3 | 250 |
| **1.3** | 2.3 | 300 |
| **1.4** | 2.6 | 300 |
| **1.5** | 2.6 | 600 |
| **1.6** | 3.0 | 250 |
| **1.7** | 3.0 | 300 |
| **1.8** | 3.0 | 400 |
| **1.9** | 4.0 | 250 |
| **1.10** | 4.0 | 280 |
| **1.11** | 4.0 | 450 |
| **1.12** | 6.5 | 250 |
| **1.13** | 6.5 | 280 |
| **1.14** | 6.5 | 400 |
| **1.15** | 6.5 | 550 |

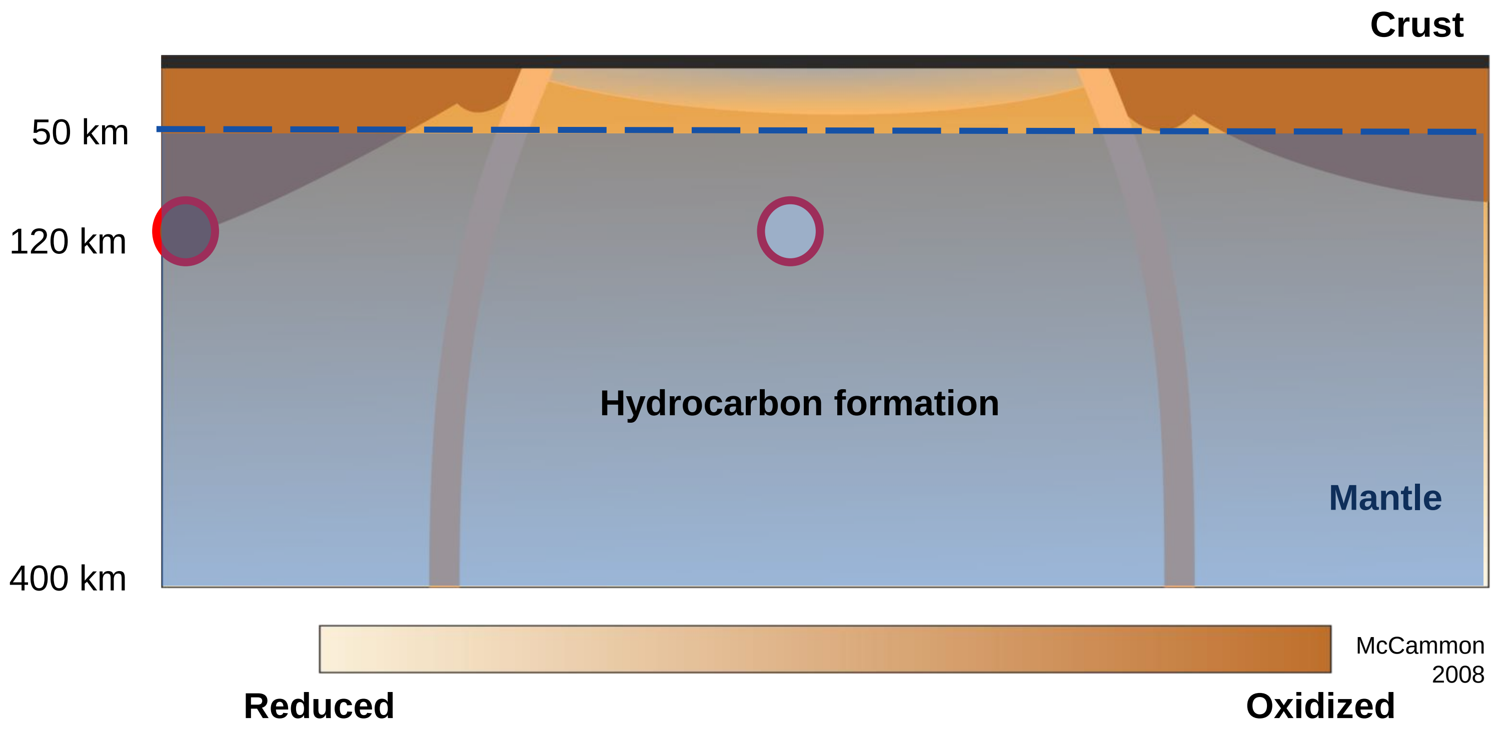


# Experimental results 2. Redox conditions



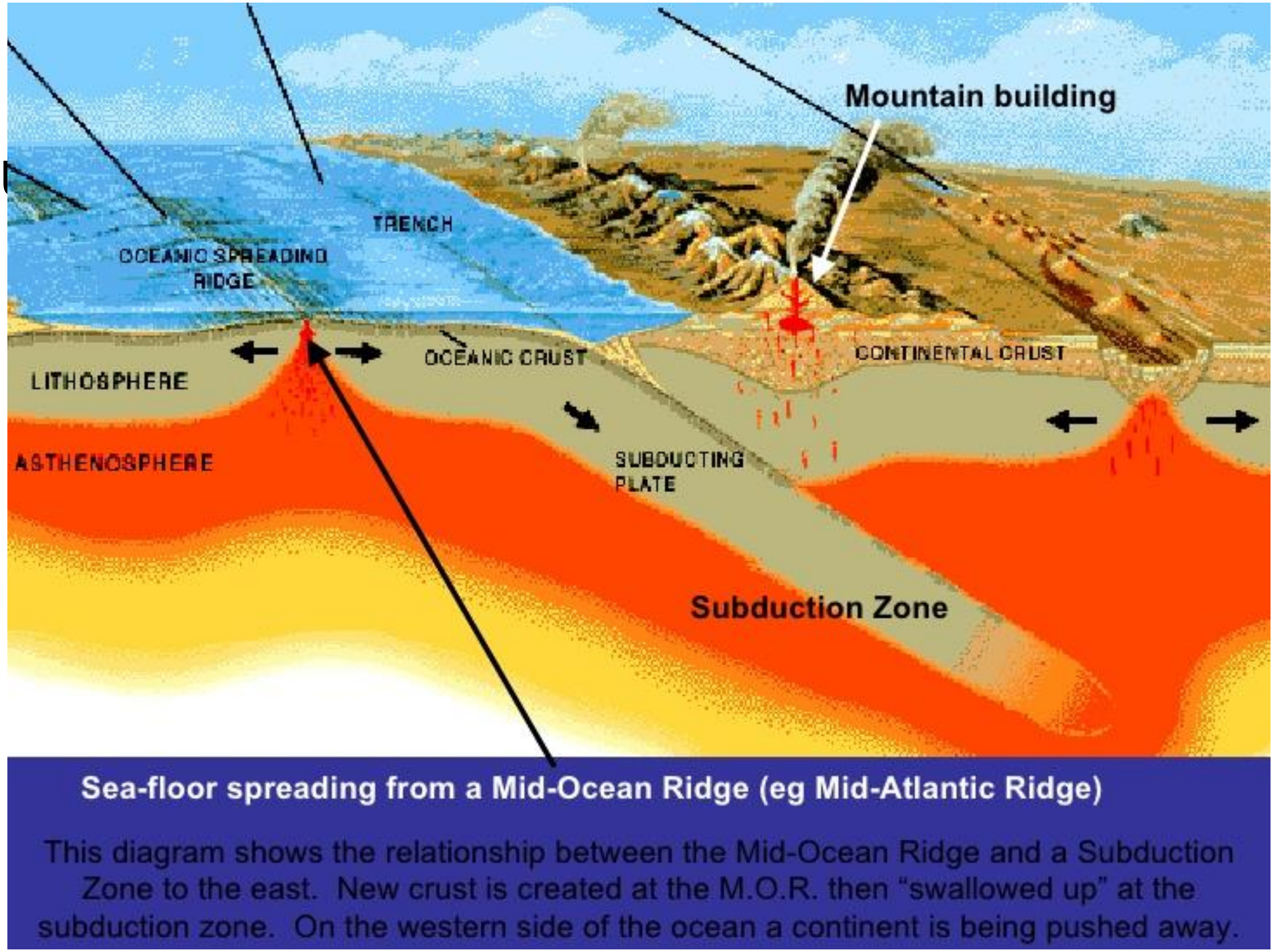
# Mid-conclusion

## Conditions of deep $CH_4$ formation




Formation of methane is possible at depth below 50 km in any mantle surroundings

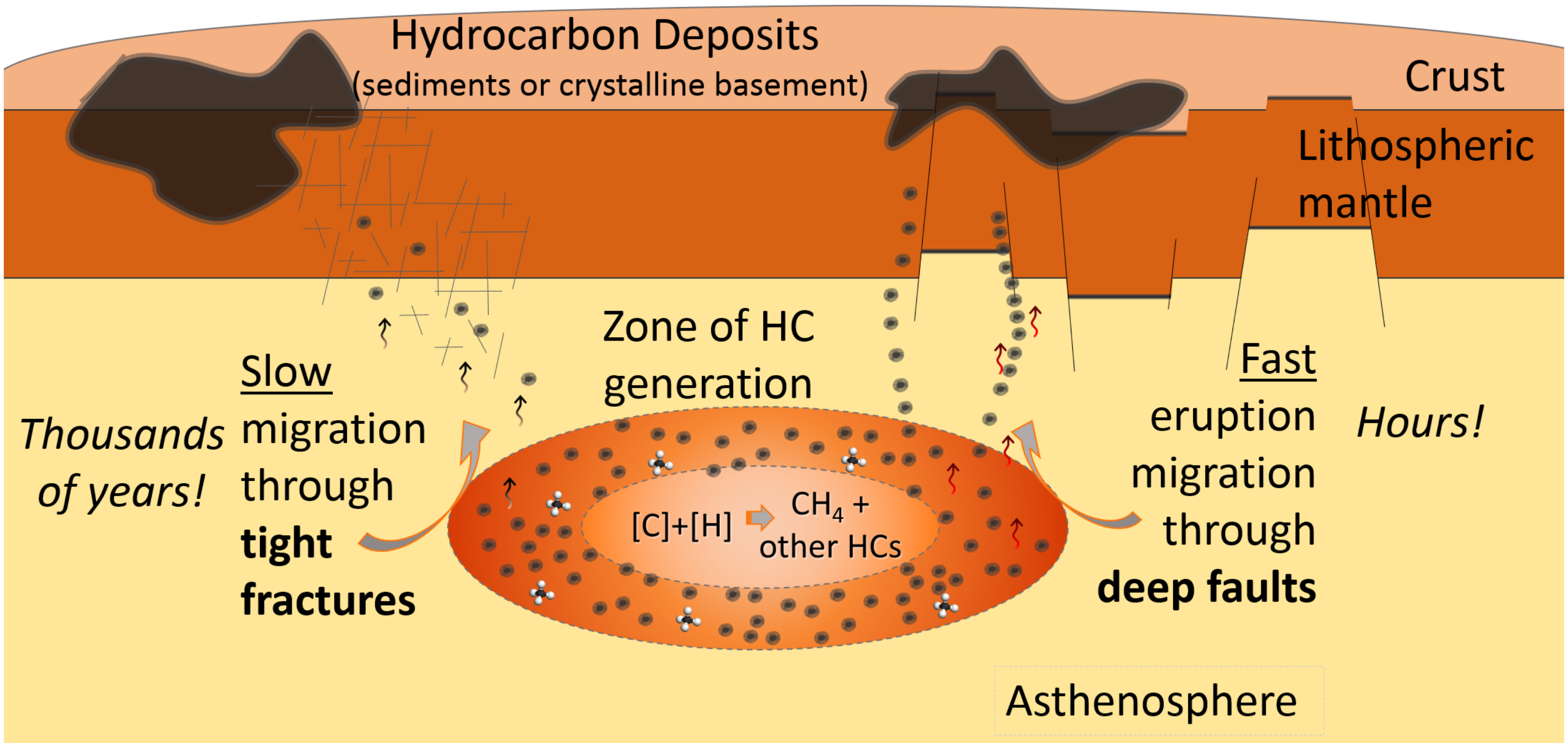
# Subdu



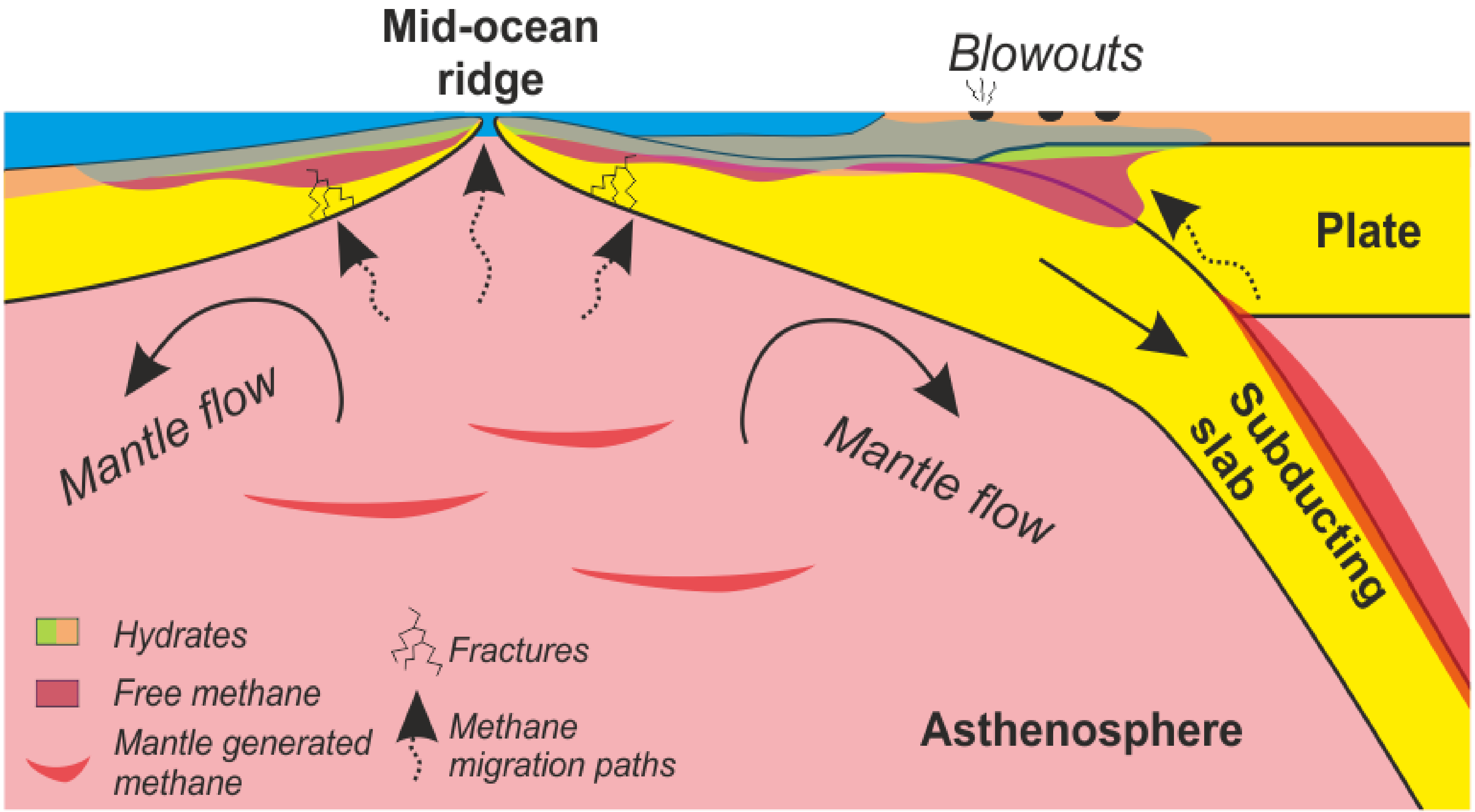
Mountain building
TRENCH
OCEANIC SPREADING RIDGE
OCEANIC CRUST
CONTINENTAL CRUST
LITHOSPHERE
ASTHENOSPHERE
SUBDUCTING PLATE
Subduction Zone
Sea-floor spreading from a Mid-Ocean Ridge (eg Mid-Atlantic Ridge)
This diagram shows the relationship between the Mid-Ocean Ridge and a Subduction Zone to the east. New crust is created at the M.O.R. then "swallowed up" at the subduction zone. On the western side of the ocean a continent is being pushed away.

# Migration paths of $CH_4$ from mantle

## Mantle



# Migration of mantle methane to ocean floor sediments

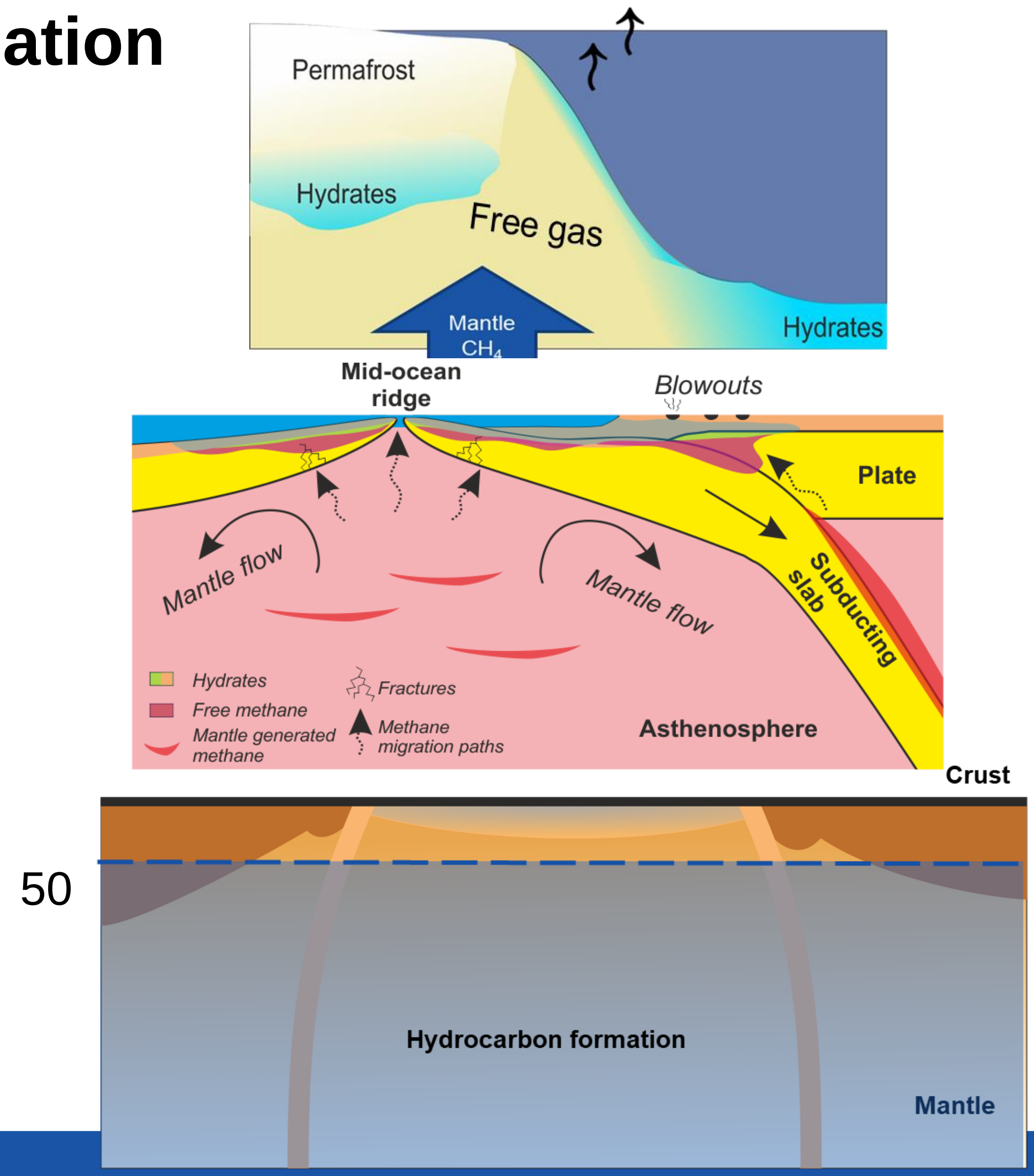



Migration of methane is possible close to the shelf, in the ocean floor sediments

# HYPOTHESIS. Contribution of mantle CH4 to hydrate formation

Methane can be generated abiogenically in mantle at depth of ~50 km and below despite redox conditions.

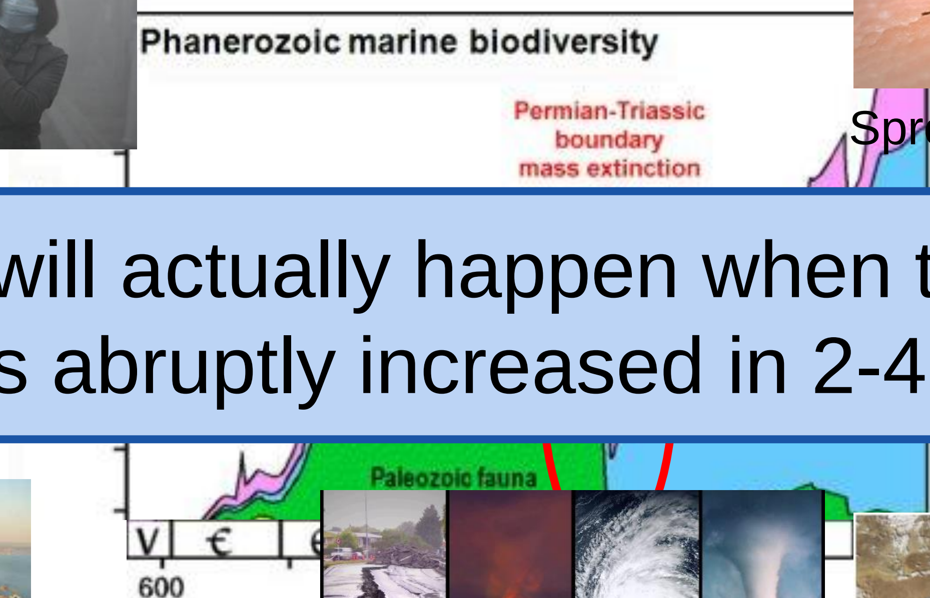
**Hypothesis**: Deep generated methane migrates up through tectonic faults, forming hydrates in marine sediments and accumulating as free gas under hydrates. This methane will eventually emit to the atmosphere during hydrates' degradation.



# Emission = Global warming

Poor air quality

Extinction ?

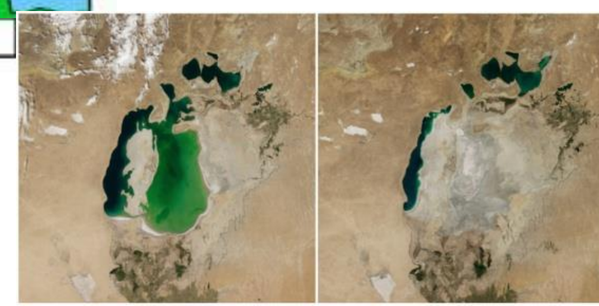



Spreading diseases

**What will actually happen when temperature is abruptly increased in 2-4-8 $^{o}$C?**

Coastal flooding

Natural disasters



Drying lakes and seas

# What is the solution?

**There is no reason to panic.**
**There is a reason to think.**


Thank you for your attention!

# Support

DEEP CARBON OBSERVATORY

GUBKIN UNIVERSITY

ГУБКИНСКИЙ УНИВЕРСИТЕТ

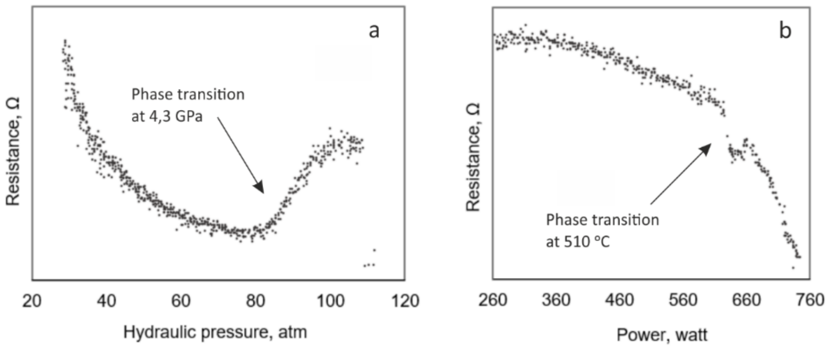
SKOLKOVO

Global Education Program

BGI

Bayerisches Geoinstitut

# Calibration??



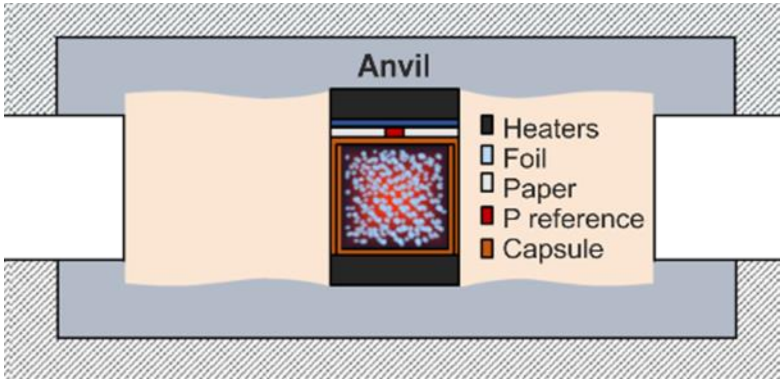
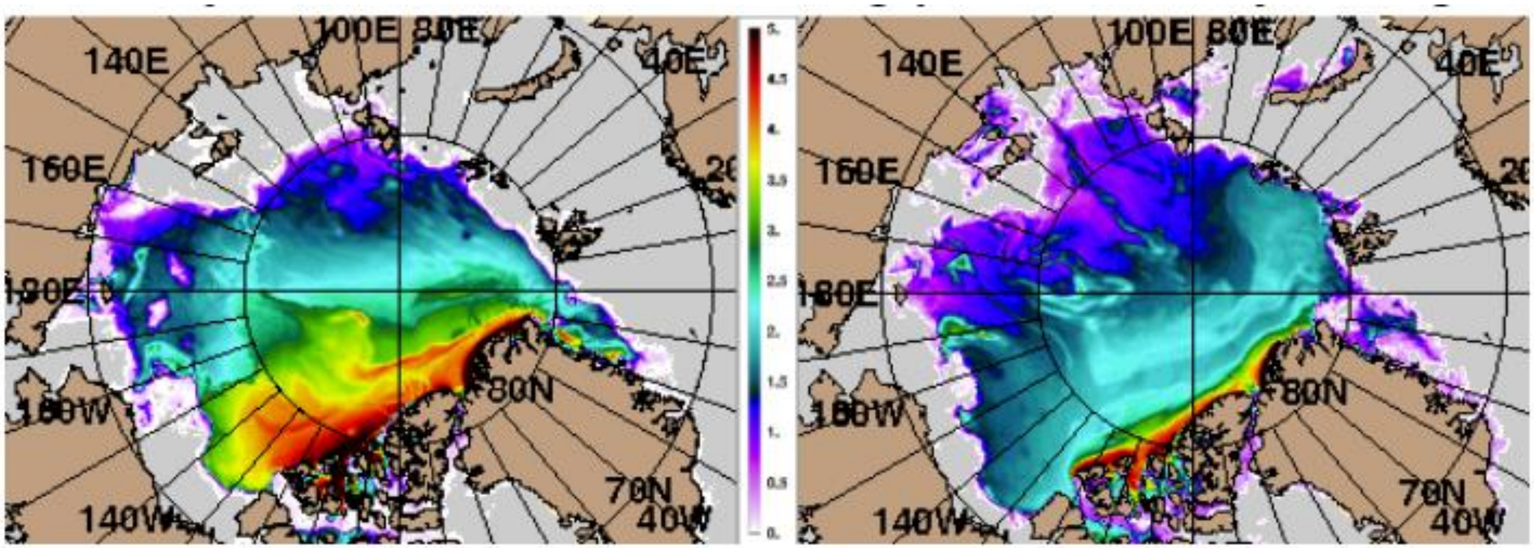




**Figure 2.4**. Representative graphics for a toroid-type high-pressure chamber calibration: **a** – pressure calibration at ambient temperature, the reference substance is PbSe, the resistance leaps after a phase transition at 81 atm of hydraulic pressure of the equipment, which applies 4.3 GPa to the sample; **b** – temperature calibration at 2.6 GPa, the reference substance is Pb, the resistance drops after a phase transition at the power of 620 watt of the equipment, which applies 510 °C to the sample [62] (appended Paper A).

# Arctic ice degradation



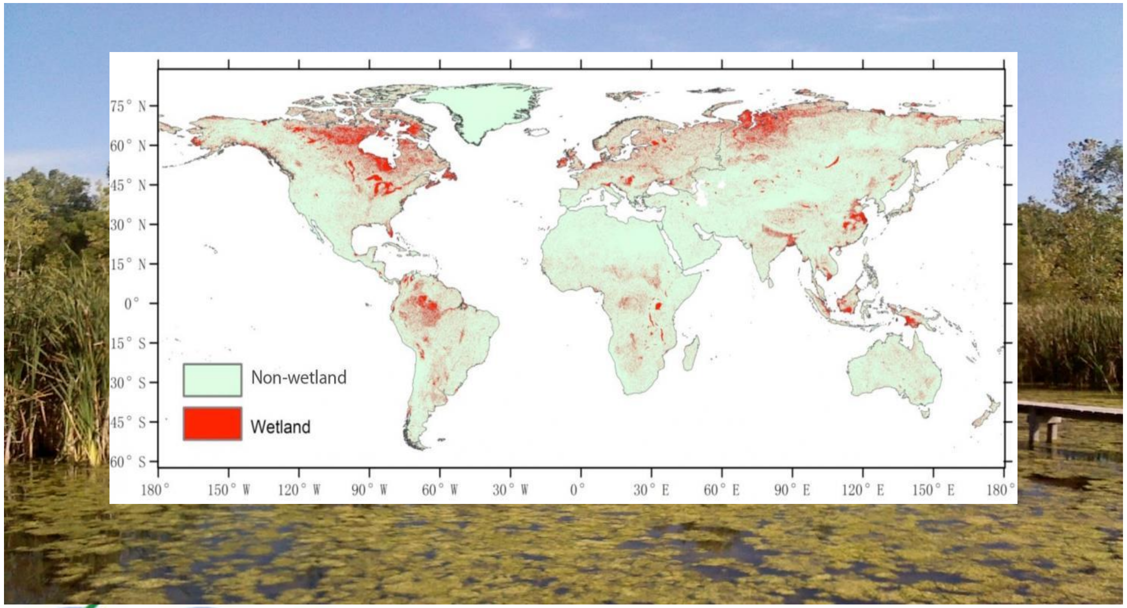

2012

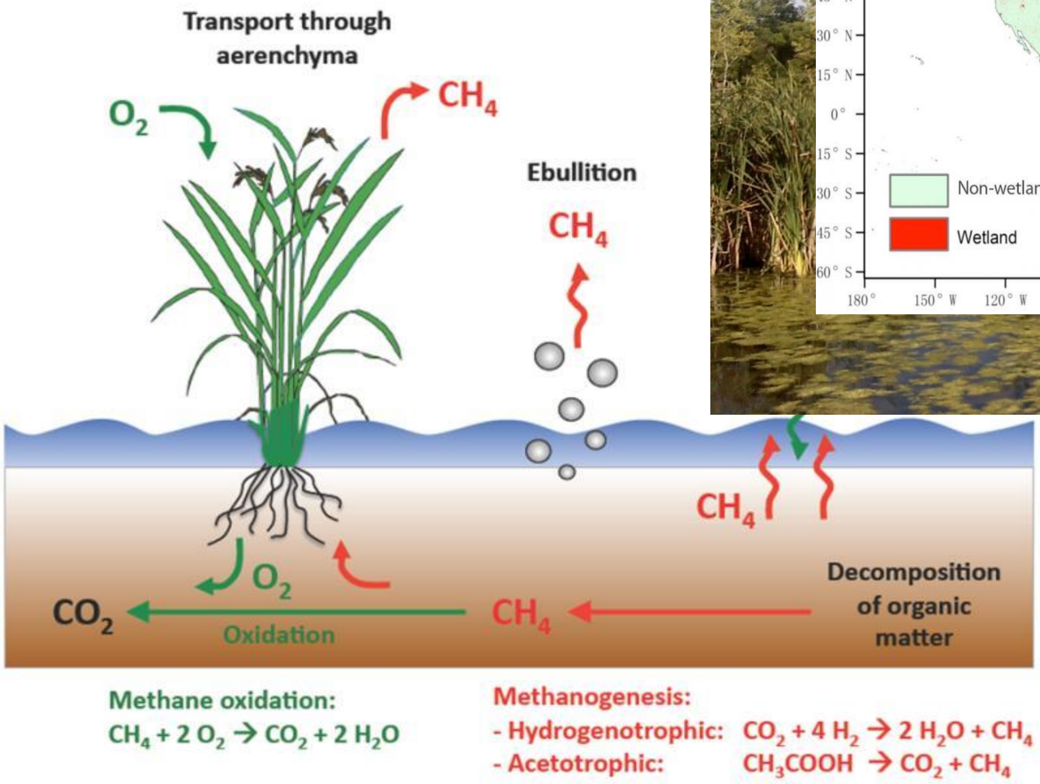
2017

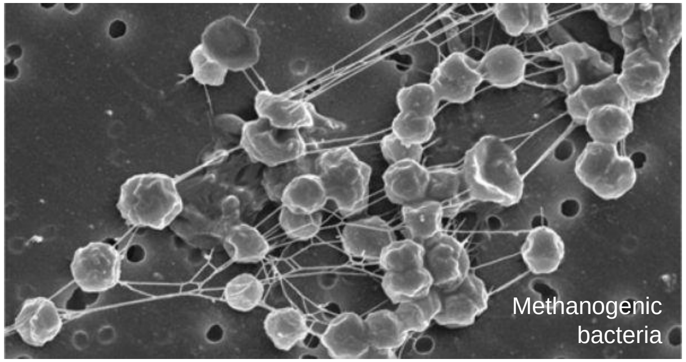
Satellite model of the thinning of ice in Arctic
Credits to Sam Carana, Arctic News

No Arctic ice in 2040?

# Methane formation in wetlands

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