

Carbonate Sedimentology



Outline of the course

- Introduction and basic concepts
 - The inorganic carbon cycle
 - The classification of carbonate rocks and sediments
 - Principles of physical oceanography
- Carbonate depositional systems
 - Carbonate factories and carbonate precipitation modes
 - Types of carbonate platform
 - Carbonate platform dynamics and principles of sequence stratigraphy
- Carbonates in the field
 - Facies analysis and mapping of carbonates
 - Examples of carbonate platforms

Course organization

- This course grants 6 credits organized in:
 - 24 hours in class or lab
 - 36 hours in the field
- Lectures will be on Mondays (11am - 13pm, room “B” bld. “O”) and Wednesday (11am – 13am, room “C” bld. “C”) of the San Giovanni campus
- Field excursions (dates to be scheduled, ideally in June):
 - one 4-days excursion to the Latemar (if possible), otherwise we will go to the field in the vicinities of Trieste.

How you'll be evaluated:

- Oral examination **50%**
- Field work deliverables **50%**

Course organization calendar

CLASSES		
	TOPIC	Date (2023)
1	Introduction	March 6
2	Precipitation of carbonates	March 13
3	Carbonate factories	March 15
4	T-type (1)	March 20
5	T-type (2)	March 22
6	C-type	March 27
7	M-type	March 29
8	Deep water carbonates	April 3
9	Petrography of carbonates (1)	April 5
10	Petrography of carbonates (2)	April 17
11	Carbonate platform geometries	April 19
12	Sequence Stratigraphy of carbonates	May 3

LAB and EXCURSIONS	
TOPIC	
Microscopy lab	
Microscopy lab	
4-days excursion Dolomites	June

This schedule is meant to give you a “big picture” of what is planned.

Changes will be possible!

What you are supposed to learn

- the processes behind the precipitation of carbonate and the formation of carbonate rocks
- the carbonate environments and the specific features of the sediment that accumulate in them
- Know the main types platform and their specific depositional geometries
- How to observe carbonates and describe them at various scales (outcrop, hand-lens, thin section...)
- You will be introduced to methods for the study of carbonates in the lab and in the field

References and text books

- These slides
- Suggested textbooks:
 - Carbonate Sedimentology - Tucker and Wright, Blackwell, 1990
 - Origin of carbonate sedimentary rocks – James and Jones, Wiley, 2016
 - Sedimentary structures and early diagenetic features of shallow marine carbonate deposits – Demicco and Hardie, SEPM Atlas series n° 1, 1994
 - Carbonate sedimentology and sequence stratigraphy - Schlager, SEPM concept in sedimentology and paleontology n° 8, 2005
 - Microfacies of carbonate rocks - Flügel, Springer-Verlag, Berlin-Heidelberg (Germany), 2004 (and subsequent editions)

How can you find me?

- By e-mail: mfranceschi@units.it
- In my room, ideally right after lectures (or write me a e-mail to get an appointment)

What are carbonates?

- Carbonate in chemistry is salt of carbonic acid (H_2CO_3)
- With the term carbonates in geology we mainly refer to **sediments and rocks mainly made of carbonate minerals**

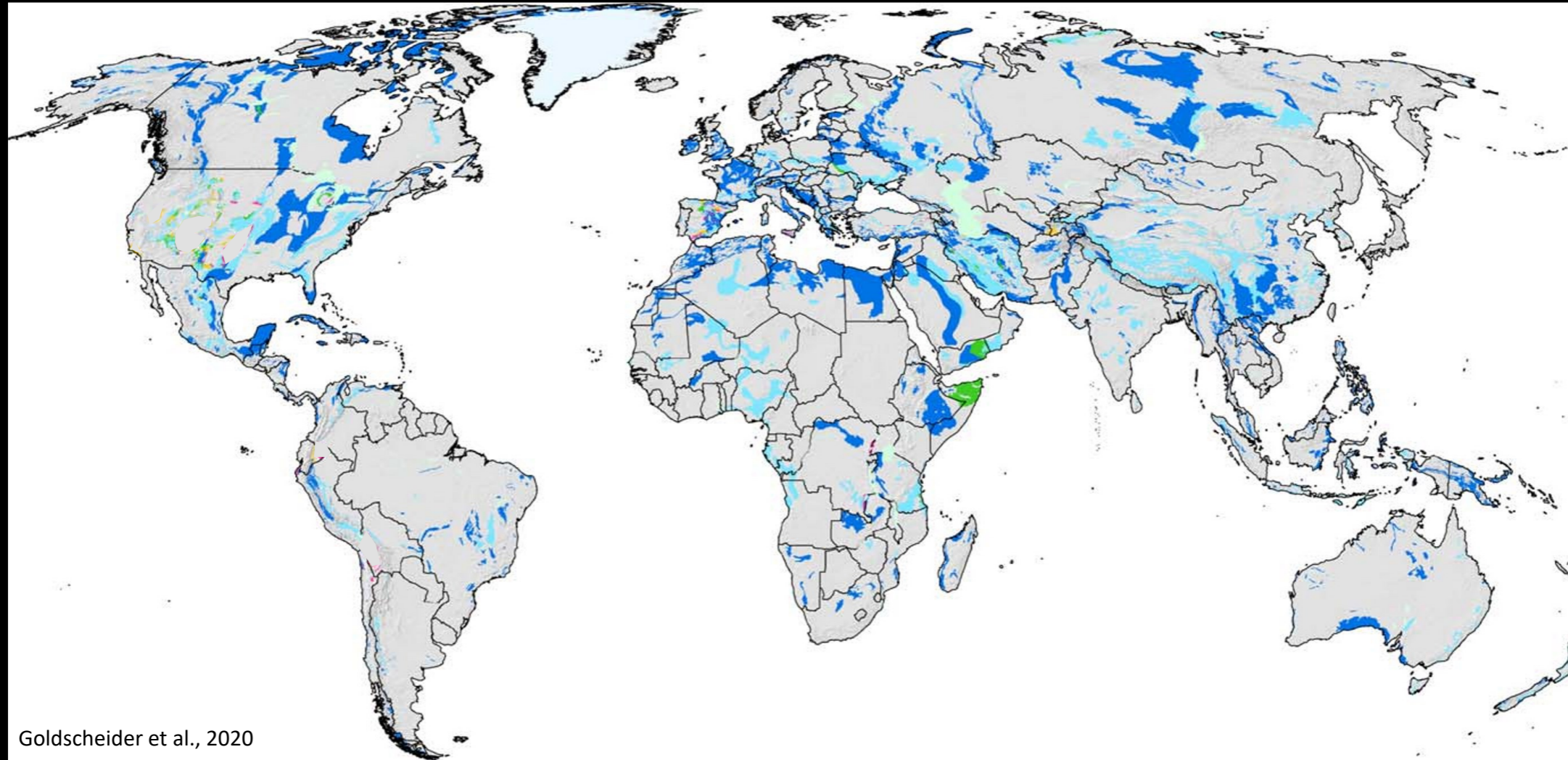





Why do we care of carbonates in geology?

- Carbonate rocks are volumetrically a most significant part of the geologic record
- Carbonates are sensitive recorders of the global marine environment. They are ecological and paleoecological archives and proxy signals for long-term and abrupt changes in the exogenic carbon cycle.
- The formation of carbonate rocks is a fundamental part of the Carbon cycle.
- Carbonate rocks possess prominent economical importance
 - Host nearly 40% of known hydrocarbons reserves
 - Contain base metal deposits (e.g. Pb, Zn)
 - May host large groundwater reservoirs
 - Are raw material for construction and chemical industry



Diffusion of carbonate rocks



-  Continuous carbonate rocks
-  Discontinuous carbonate rocks
-  Mixed carbonate and evaporite rocks

Carbonate rocks are widely outcropping across the globe. They are extensively quarried as raw material for construction and chemical industries. Large volumes of carbonate rocks also exist in the subsurface and can host important hydrocarbon and groundwater reservoirs.

Origin of carbonates



Image from nasa.gov



Fiji. Satellite image from nasa.gov

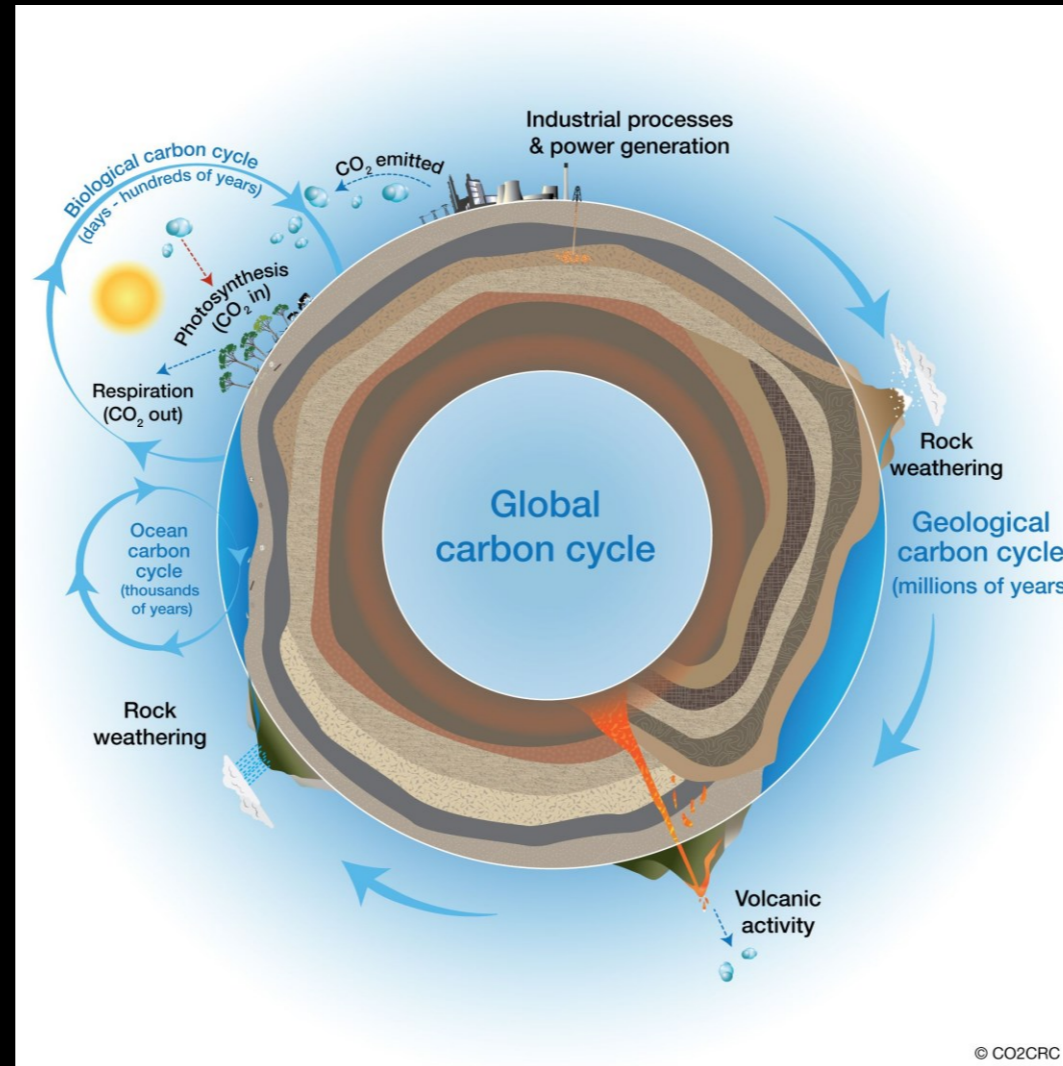


1 CM

The carbon cycle

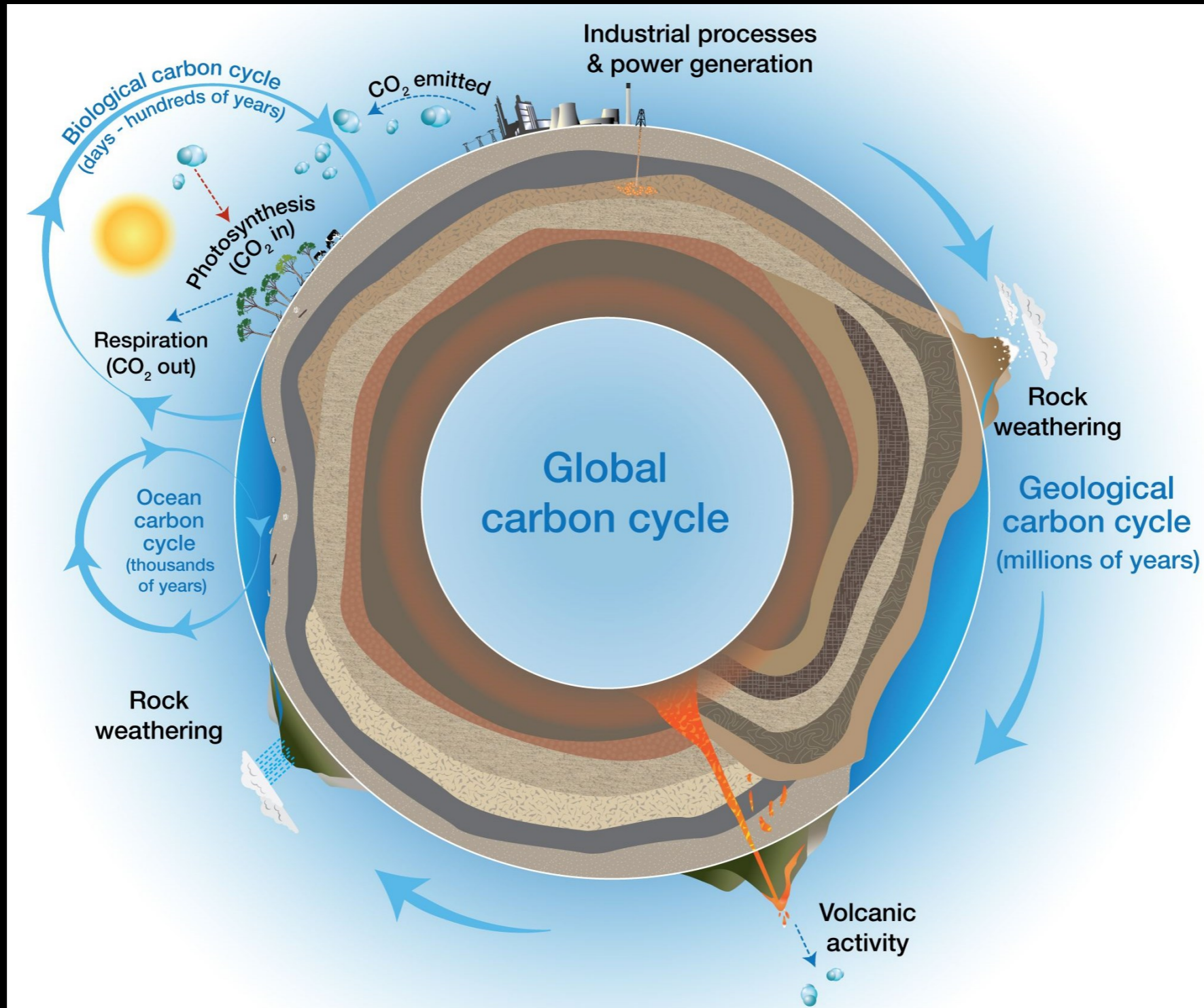
Carbonates exist because of the existence of the **carbon cycle** and, more specifically, of the **inorganic carbon cycle**

The C-cycle is a **biogeochemical cycle** in which carbon is exchanged among the biosphere, the geosphere, the atmosphere and the hydrosphere



The carbon cycle is a complex phenomenon that operates on different time scales. The formation of carbonate rocks and sediments regards more specifically the C-cycle on timescales ranging from 10^3 – 10^6 yr.

The C-cycle



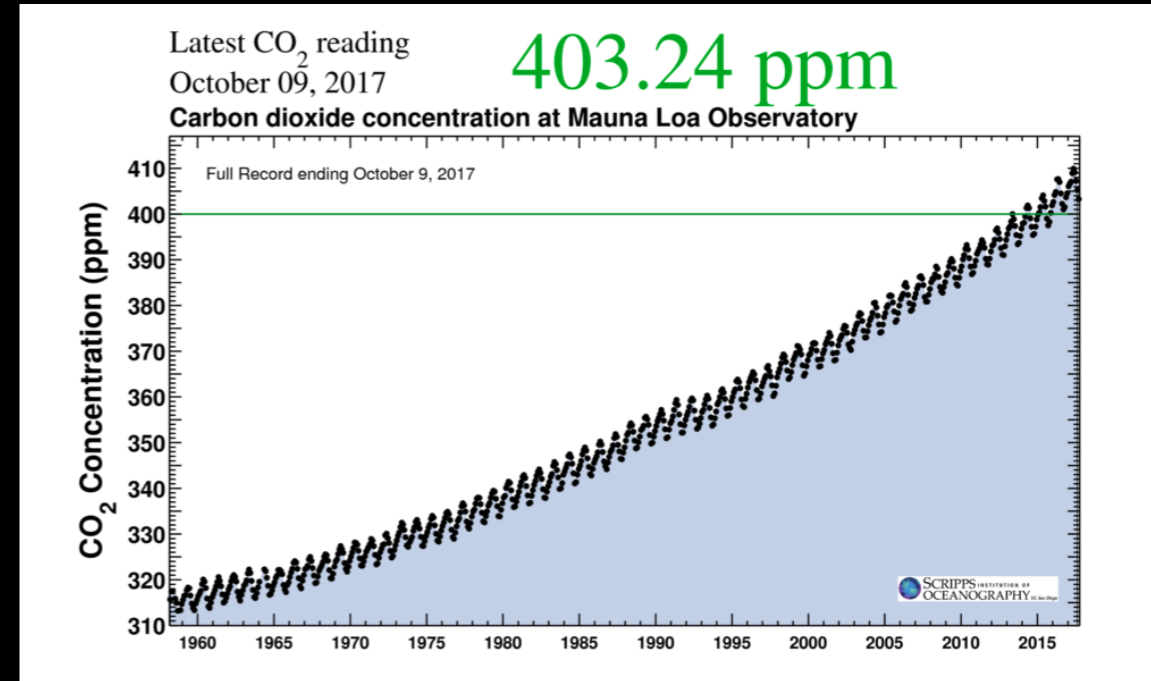
The inorganic carbon cycle

The **partial pressure**, or **concentration**, of CO₂ in the surface water of the oceans and in the atmosphere are roughly in equilibrium on a short (weeks) time scale.

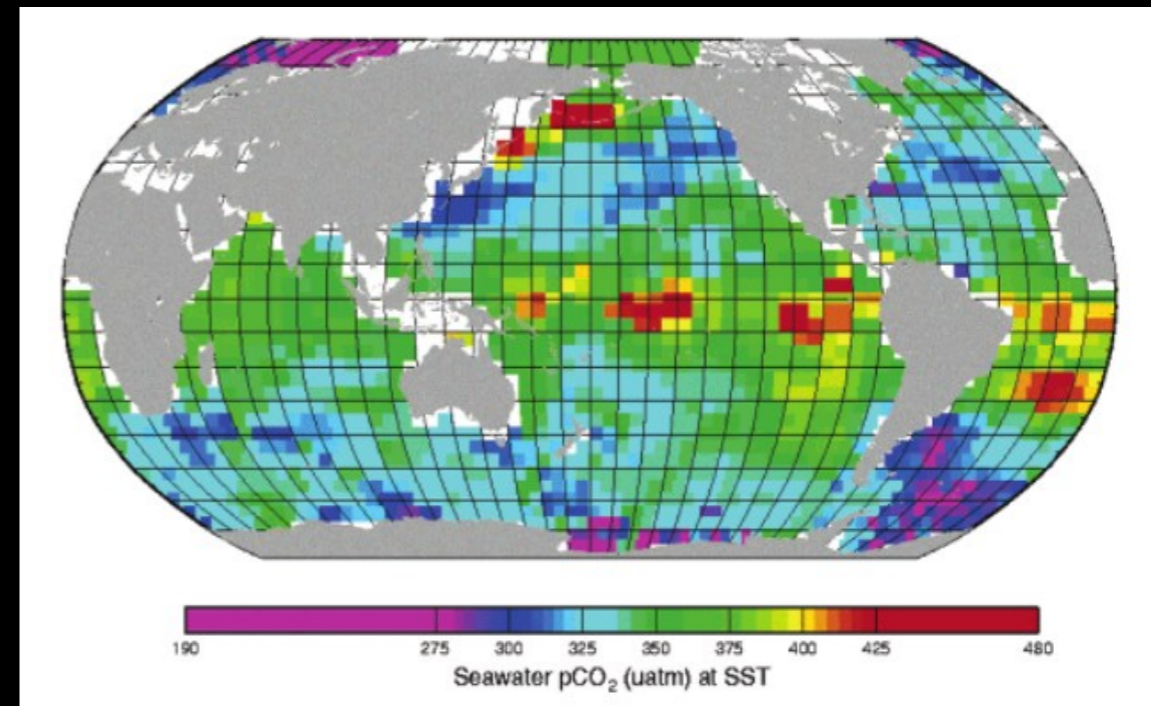
$$p\text{CO}_2 \equiv [\text{CO}_2]$$

The concentration of Carbon Dioxide in the atmosphere is rising, and is now > 400 ppm. Hydrolysis of silicates consumes excess CO₂ in the atmosphere, but it is a slow process that occurs in times of the order of tens of thousands of years (long-term feedback).

Concentration of CO₂ in the atmosphere compares well with the average pCO₂ of oceans' surface waters (from Millero, 2007, Chem. Rev., 107:308-341).



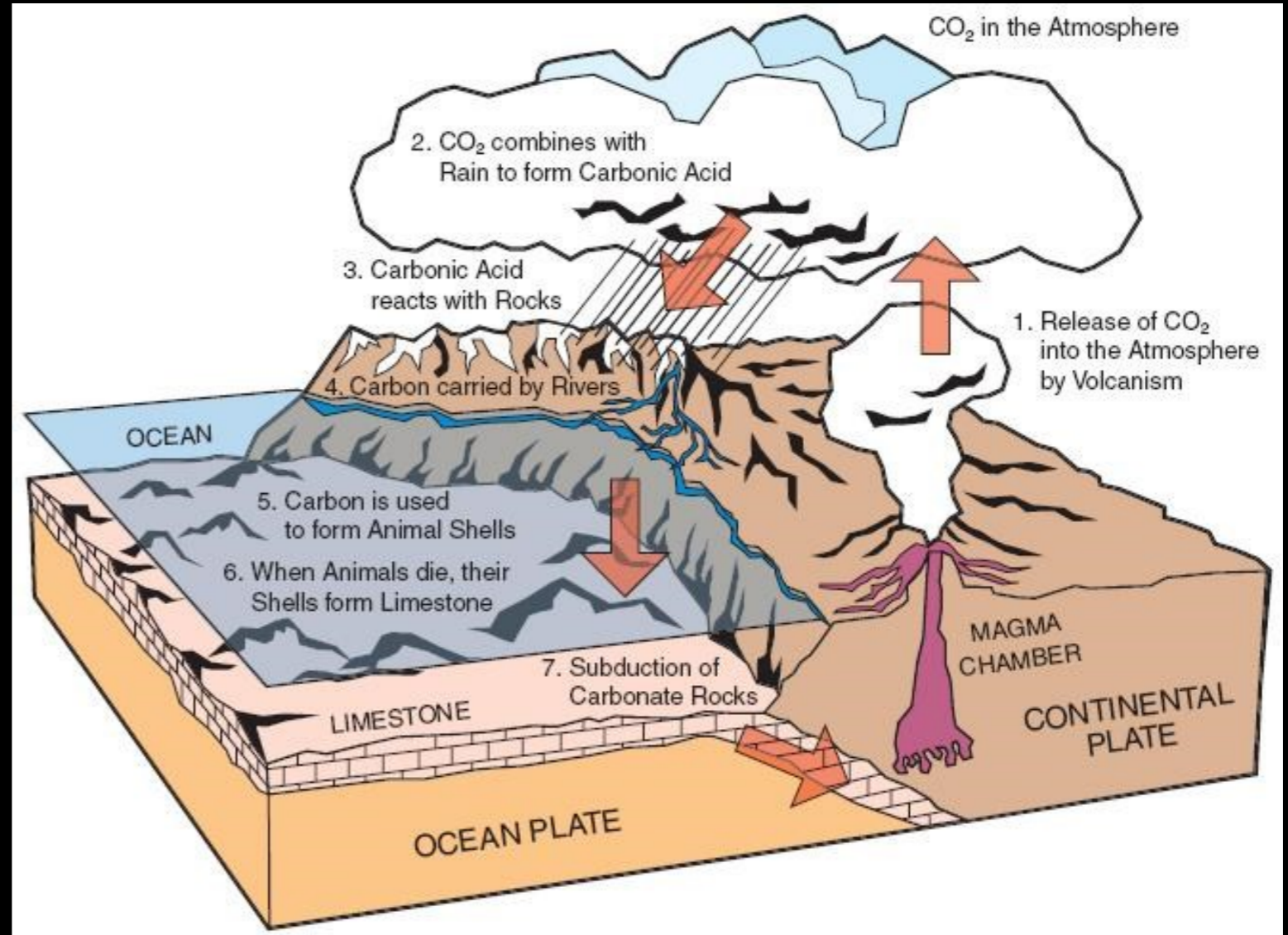
<https://scripps.ucsd.edu/programs/keelingcurve/>



The inorganic carbon cycle

With the term **inorganic carbon** we refer to the carbon that is found primarily in compounds such as carbon dioxide (CO_2), carbonic acid (H_2CO_3), bicarbonate (HCO_3^-), and carbonate (CO_3^{2-})

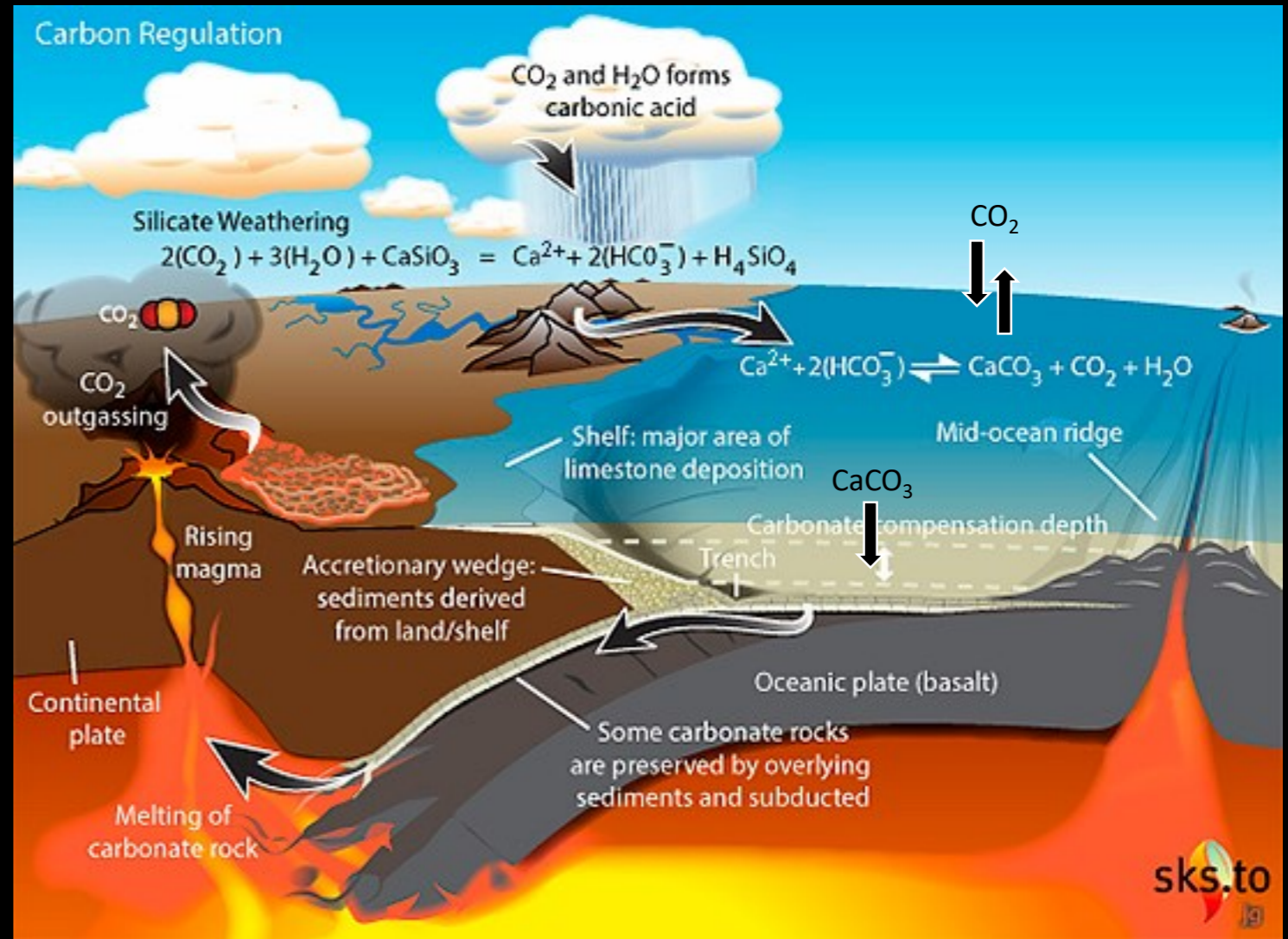
The formation of carbonate rocks and sediments is a **fundamental part** of the inorganic carbon cycle



The inorganic carbon cycle

With the term **inorganic carbon** we refer to the carbon that is found primarily in compounds such as carbon dioxide (CO_2), carbonic acid (H_2CO_3), bicarbonate (HCO_3^-), and carbonate (CO_3^{2-})

The formation of carbonate rocks and sediments is a **fundamental part** of the inorganic carbon cycle



The inorganic carbon cycle

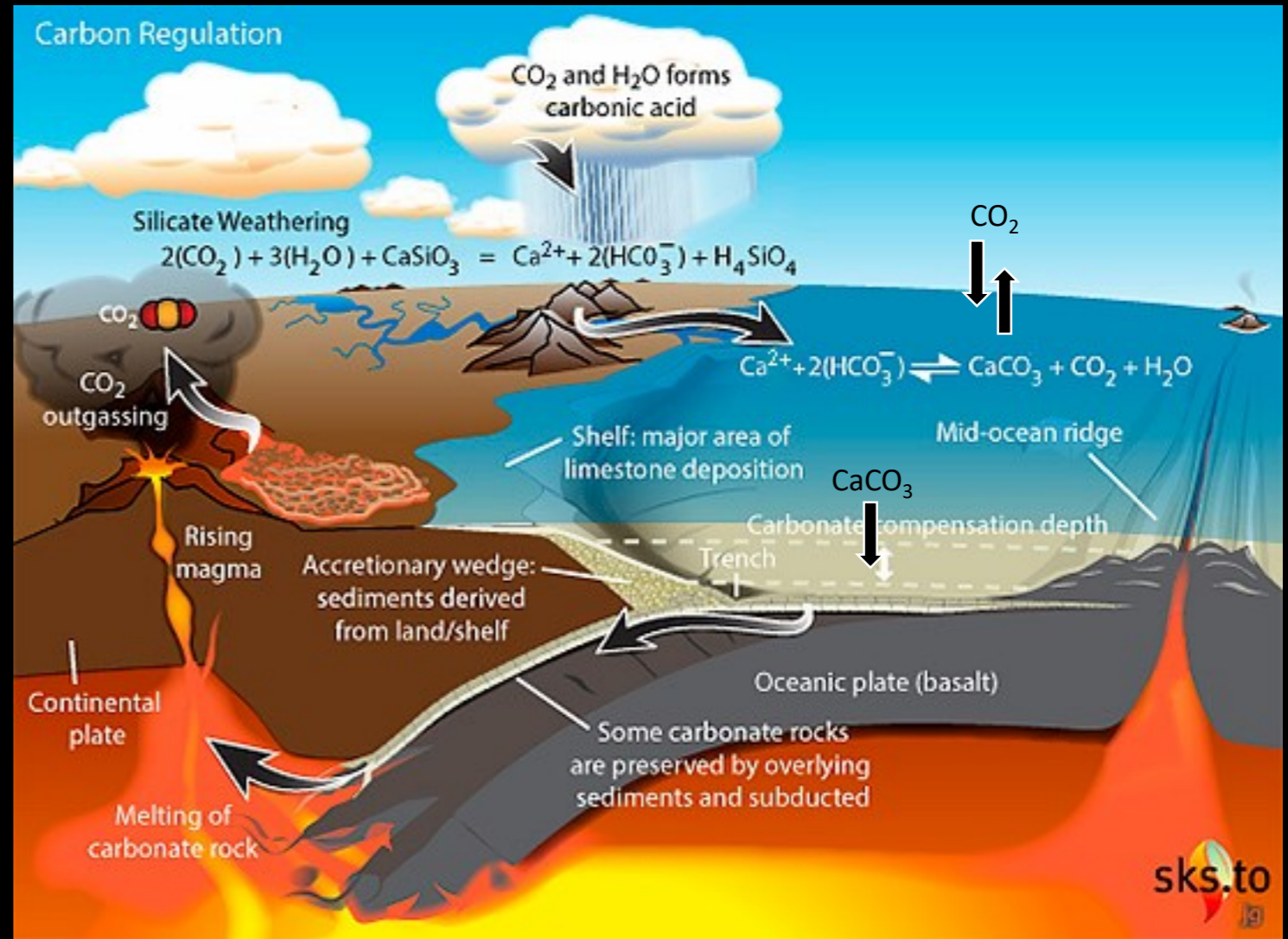
Carbon enters seawater in two ways:

- As CO_2 from the atmosphere
- As **carbonate** (CO_3^{2-}) and **hydrogen carbonate** (HCO_3^-) ions with **runoff** (e.g., rivers)

Carbon leaves seawater as **calcium carbonate** (CaCO_3) in sediments

When carbonate rocks are **subducted** the stored carbon is ultimately **released as volcanic CO_2**

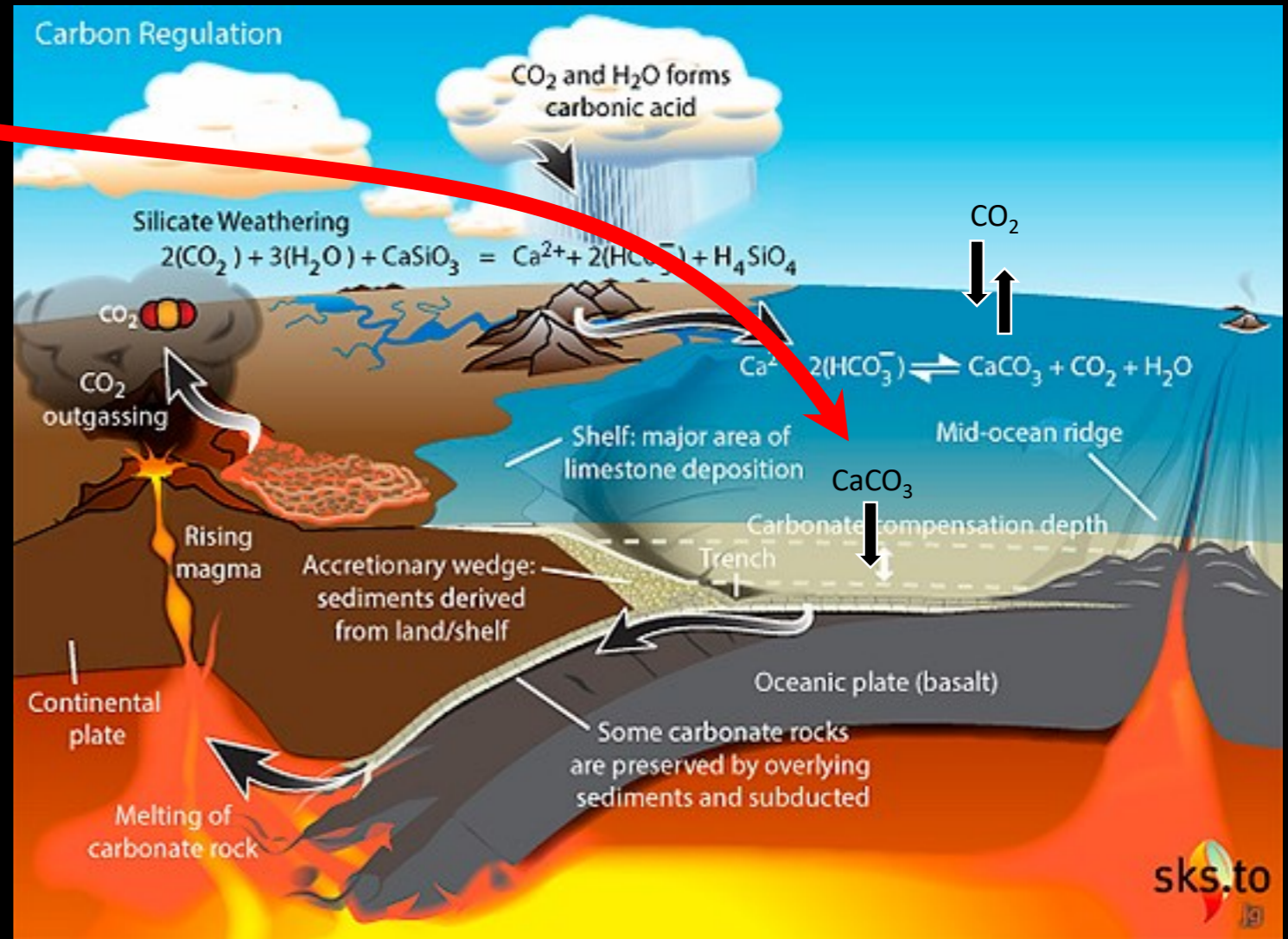
CO_2 then participates to **silicate weathering** (e.g. anortite weathers in kaolinite) and is transferred to oceans as carbonate ions through **runoff**... and the loops starts again



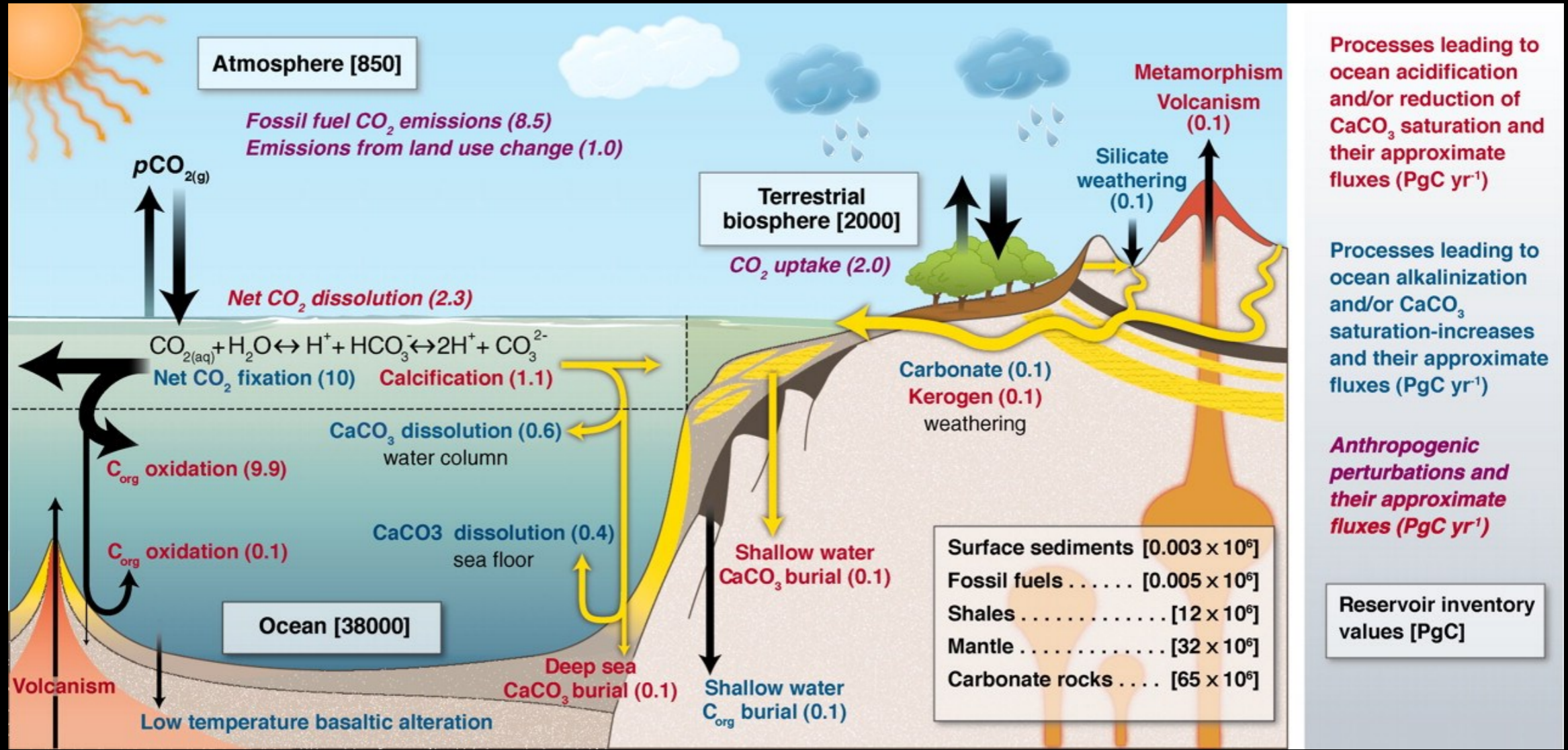
The inorganic carbon cycle

The majority of carbonates precipitate in the oceans and form carbonate sediments and ultimately, through lithification, become carbonate rocks

Although carbonates can form also in continental environments and freshwater, this latter type of carbonates is minor in terms of volumes (but still very important).



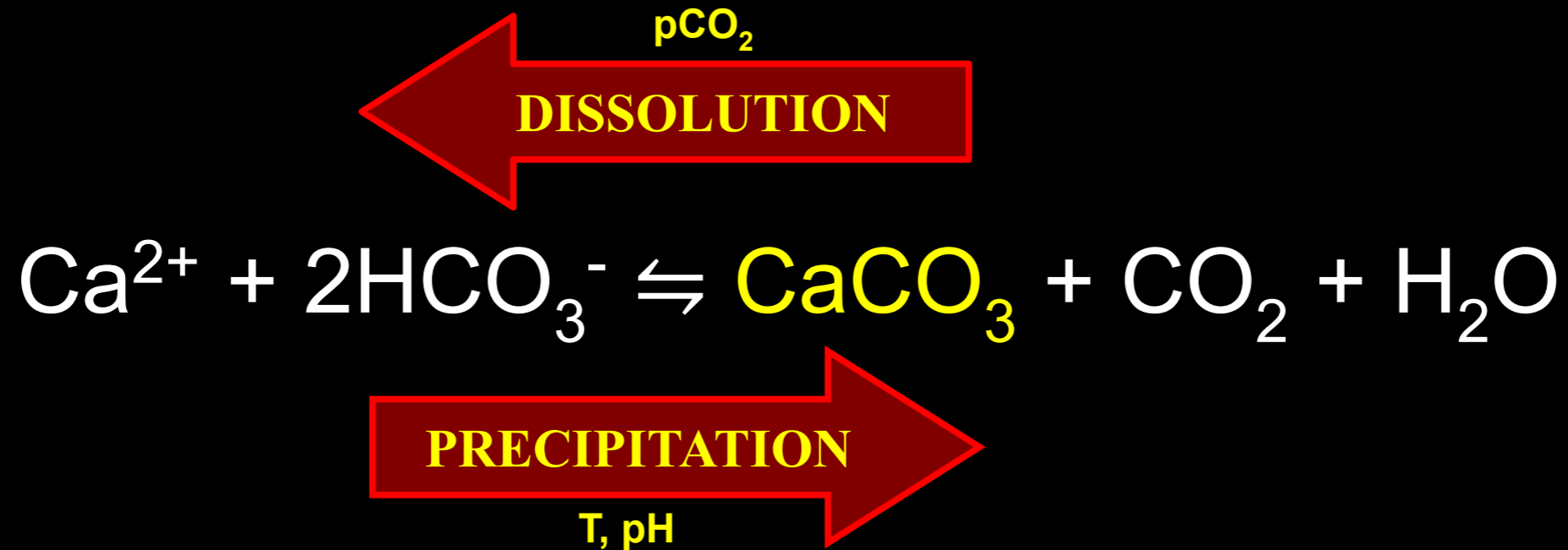
To have an idea of the actual C fluxes involved....



The carbon cycling in the oceans according to Hönisch et al., 2012.

1 Pg = 10¹² Kg

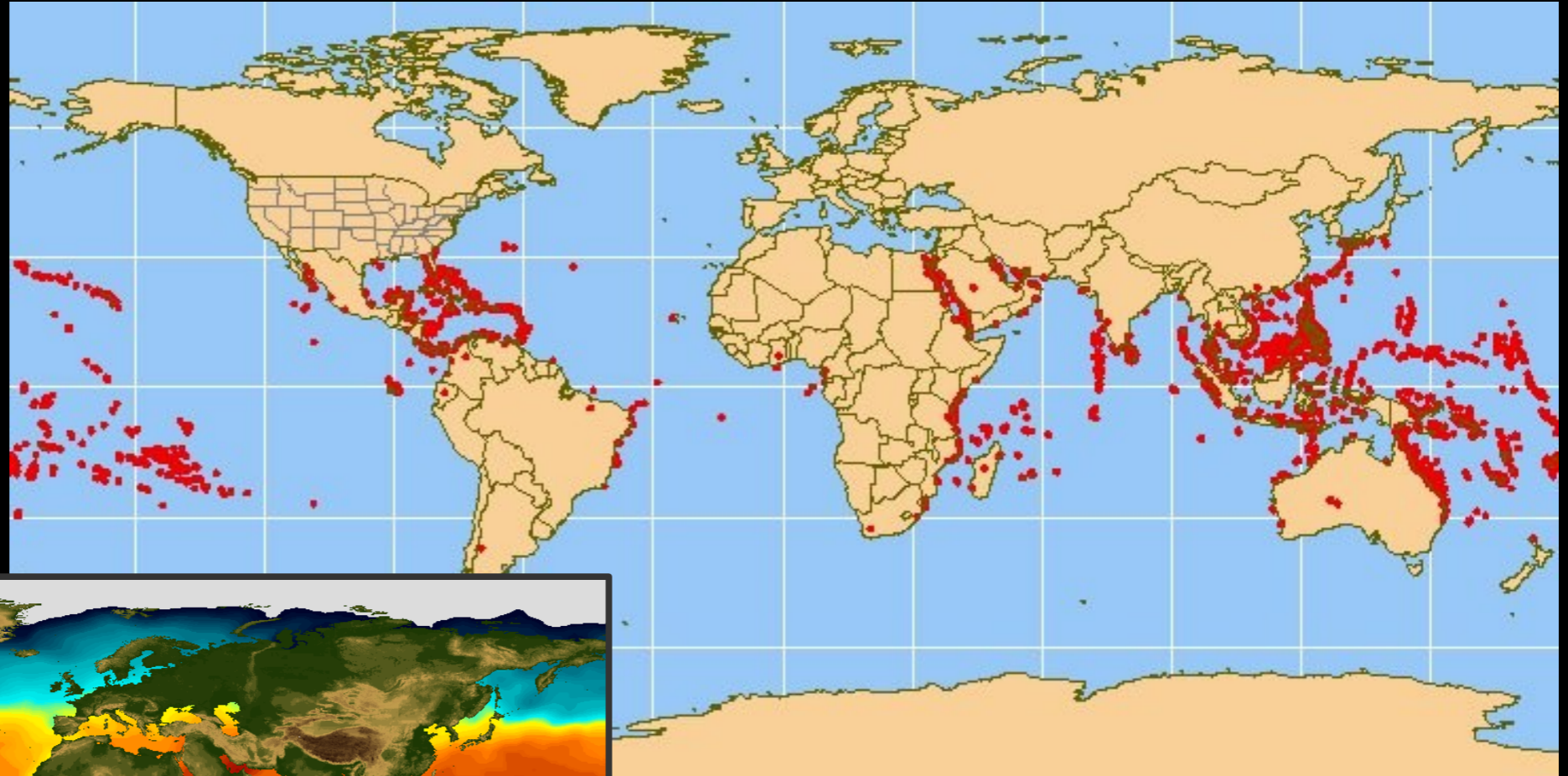
The carbonate dissolution – precipitation equilibrium reaction



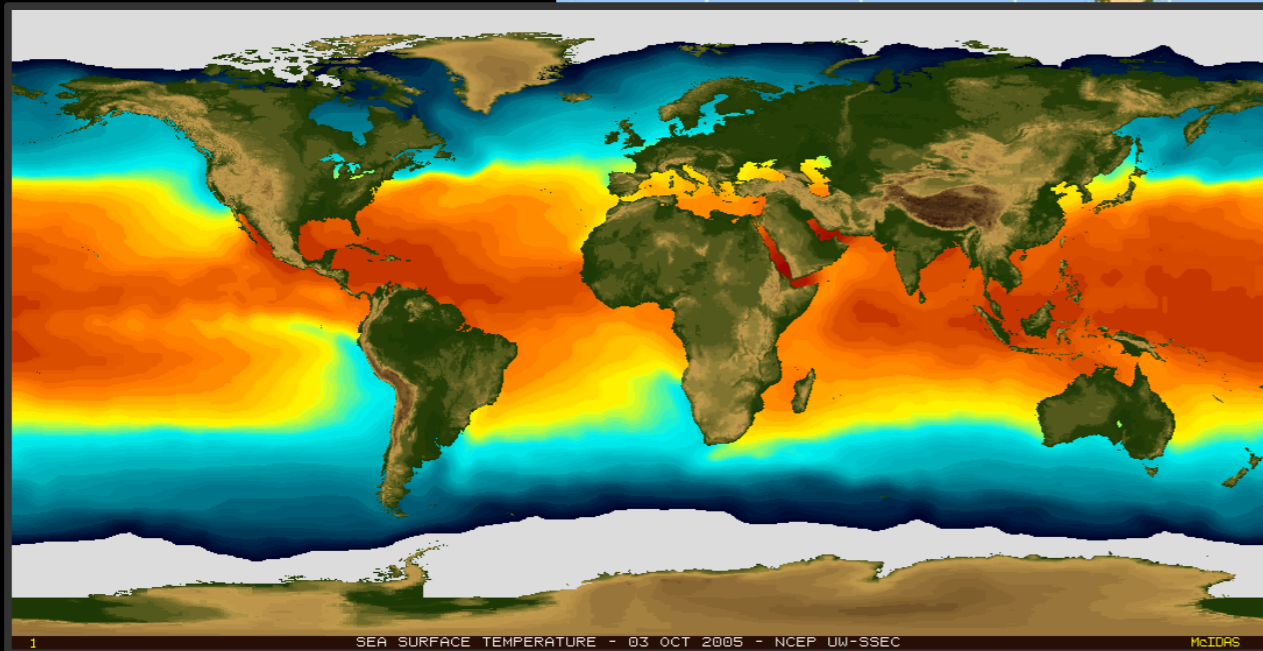
The dissolution-precipitation reaction is an equilibrium reaction which equilibrium constant changes in function of (mostly):

- **T**: Carbonate is precipitated as temperature rises.
- **pH**: Carbonate is precipitated as pH rises.
- **pCO₂**: Carbonate is dissolved as pCO₂ rises.

Controls on carbonate precipitation

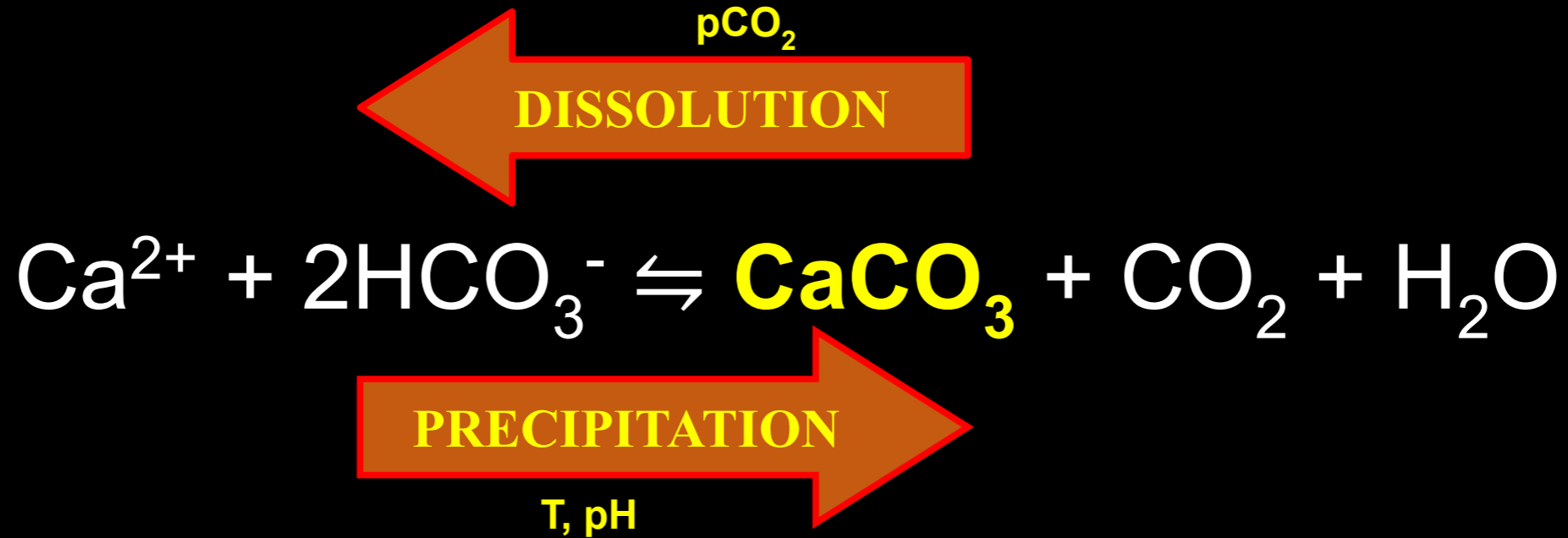


World distribution of coral reefs
(<http://www.coralreef.noaa.gov/>)



Global ocean surface temperature
(<http://www.ssec.wisc.edu/data/sst/>)

Controls on carbonate precipitation



pCO₂, T and pH influence the reaction.

Furthermore, a major controller is **seawater saturation state with respect to carbonate (Ω)**

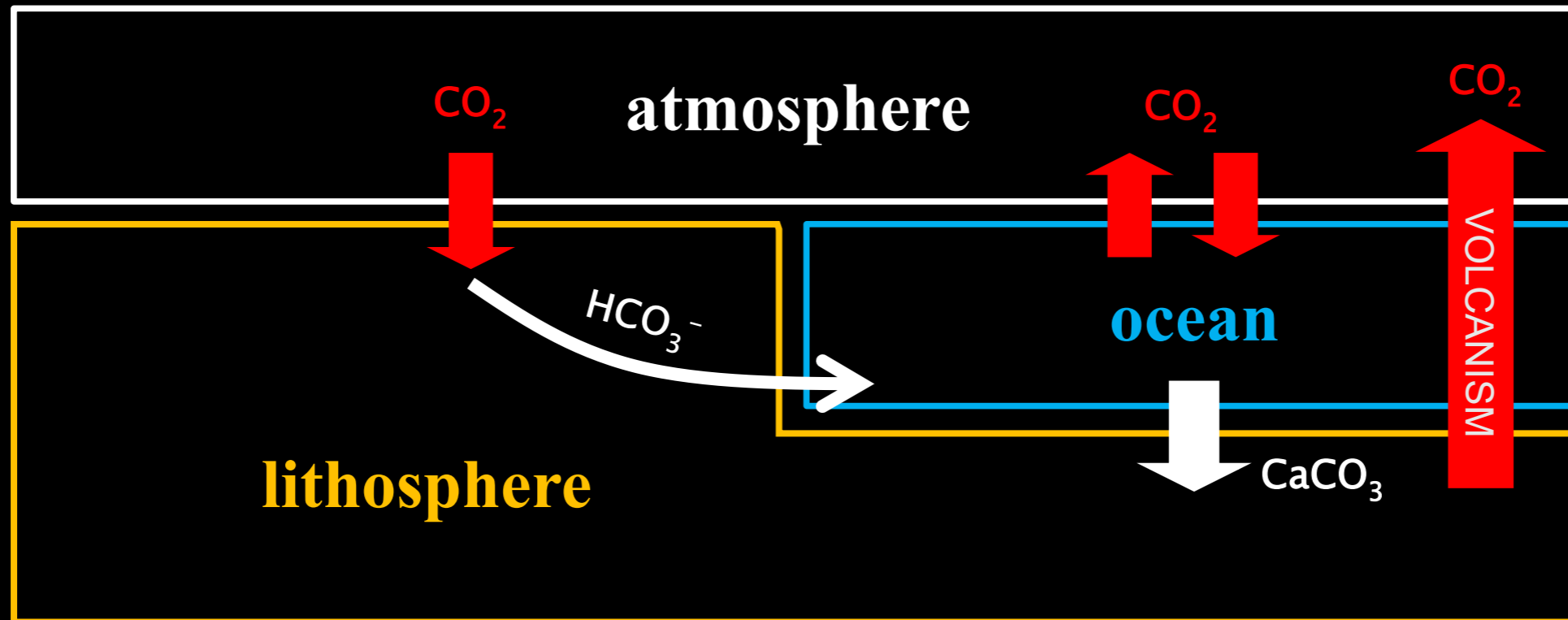
ION CONCENTRATIONS

$$\Omega = \frac{[\text{Ca}^{2+}]_{\text{sw}} \times [\text{CO}_3^{2-}]_{\text{sw}}}{K_{\text{sp}}^*}$$

REACTION CONSTANT

The **saturation state** of seawater with respect to carbonate, **Ω**, indicates whether sea water tends to precipitate CaCO₃ (**Ω > 1; supersaturation**) or to dissolve CaCO₃ (**Ω < 1; undersaturation**).

Let's have a closer look to the chemistry involved in the cycle

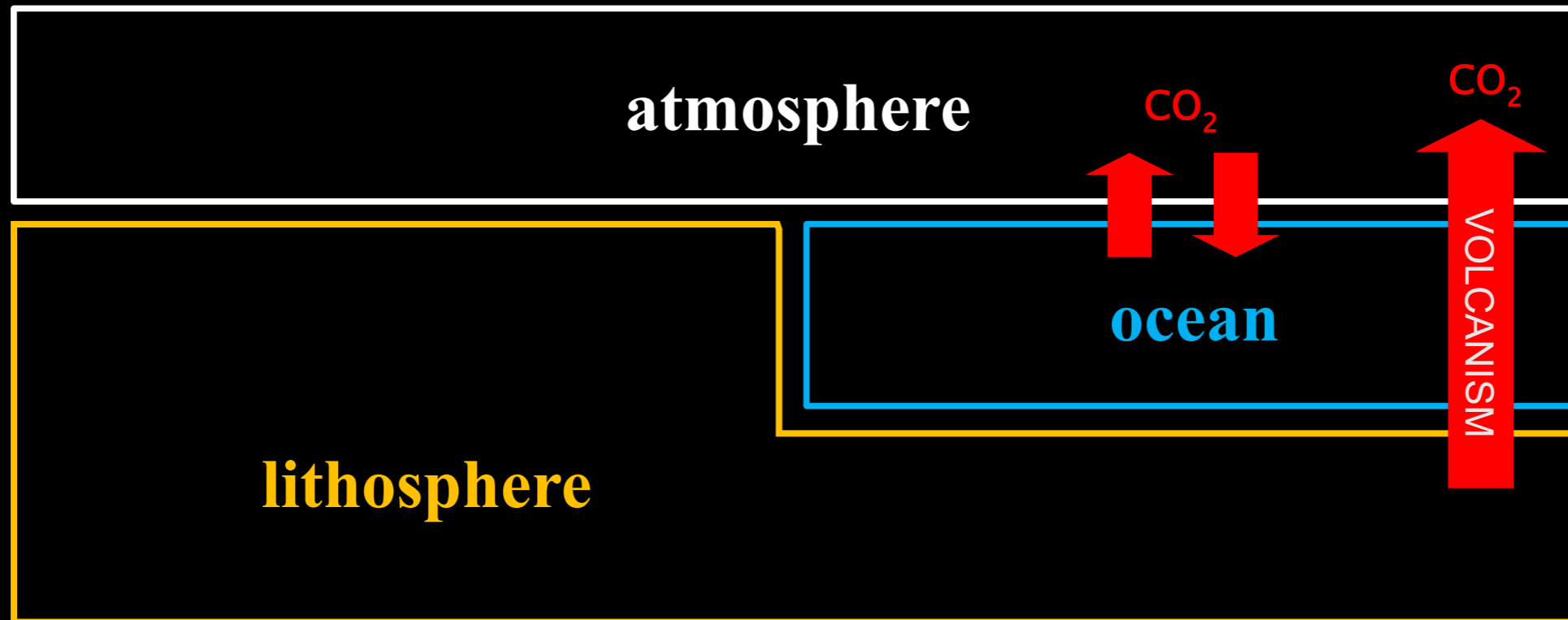


Let's have a closer look to the chemistry involved in the cycle



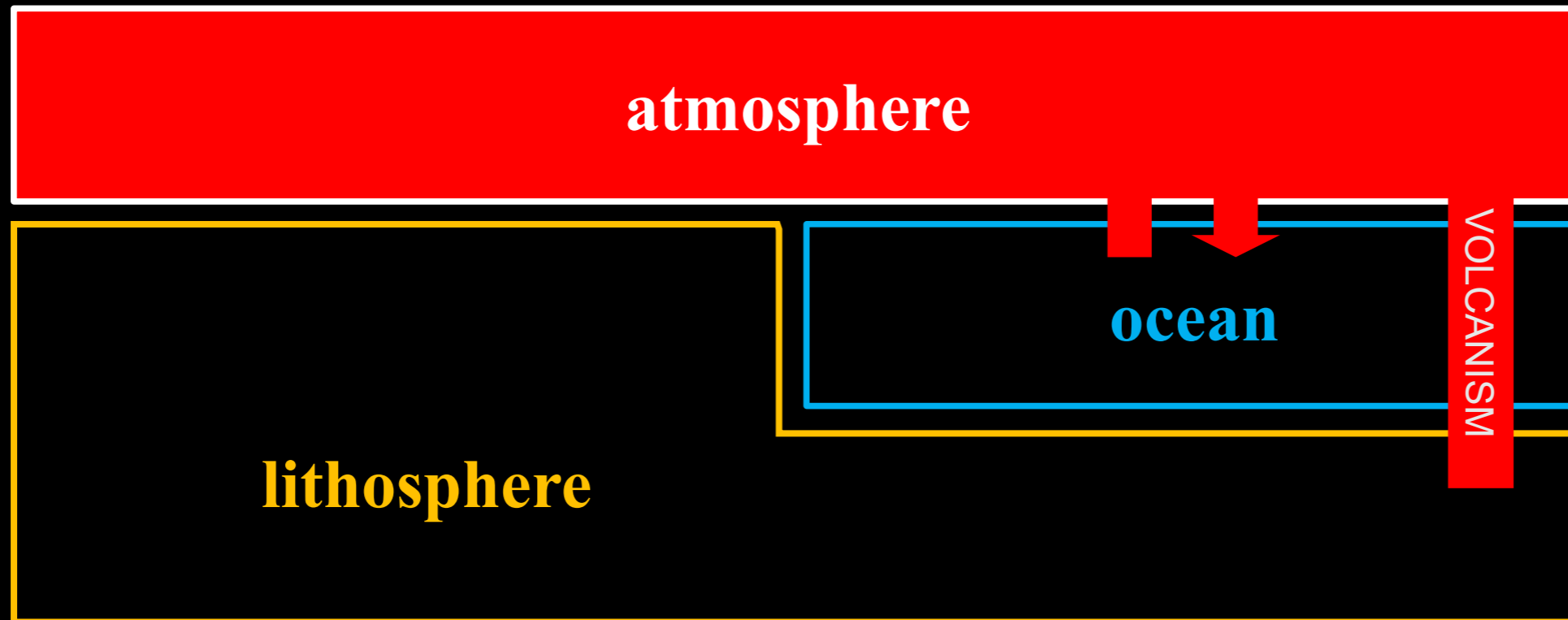
Looking at these two reactions we note that **hydrolysis of silicates consumes two carbons**, while **only one carbon is released back when carbonates precipitate**. Therefore, in the long run, the silicate/carbon cycle consumes CO_2 in the atmosphere and transfers it to the lithosphere.

The inorganic carbon cycle: a powerful mechanism that regulates climate.



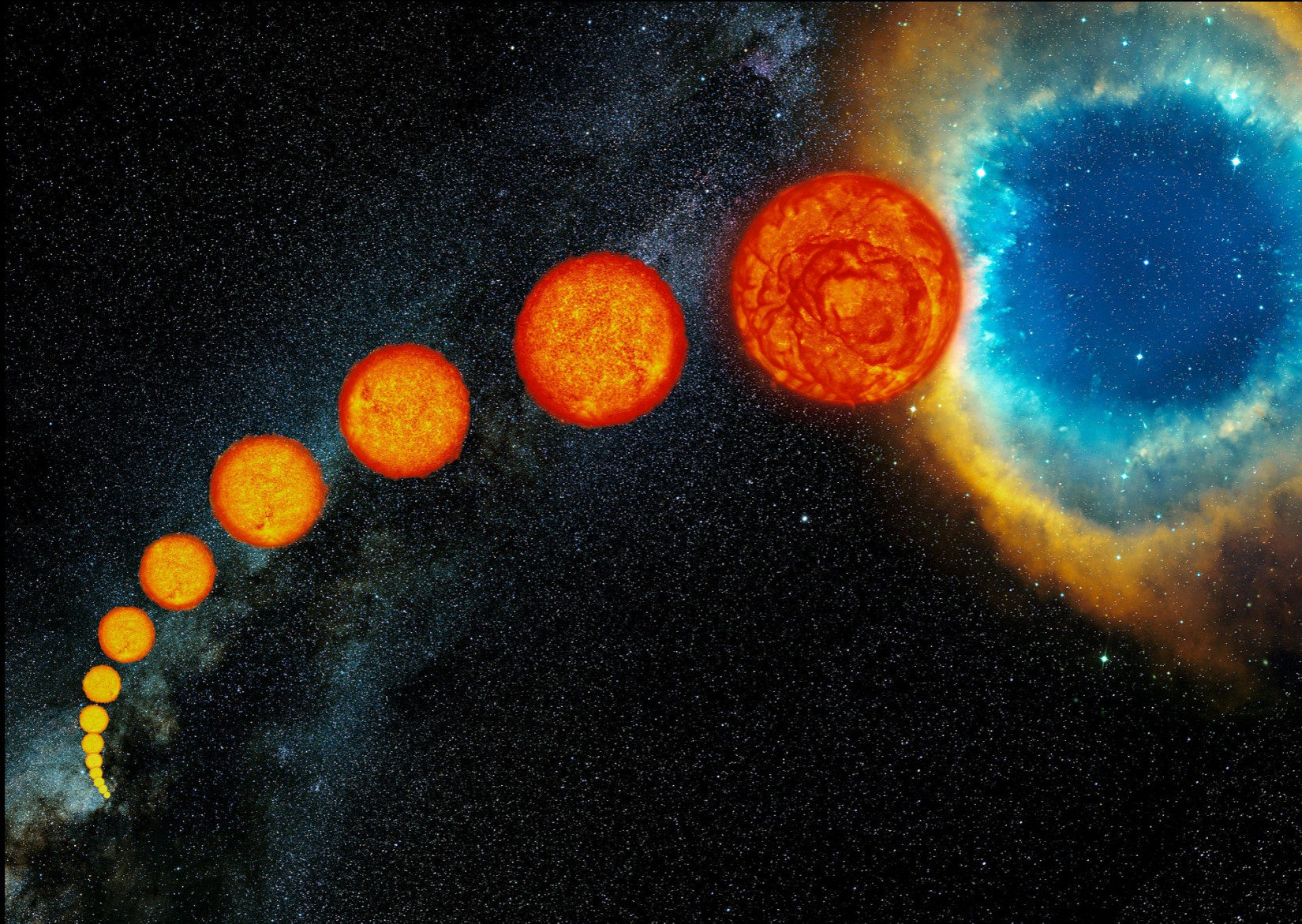
The inorganic carbon cycle: a powerful mechanism that regulates climate.

Without this mechanism, concentrations of CO₂ emitted by volcanoes would keep rising and, among many other consequences, this would cause extremely strong greenhouse effect.



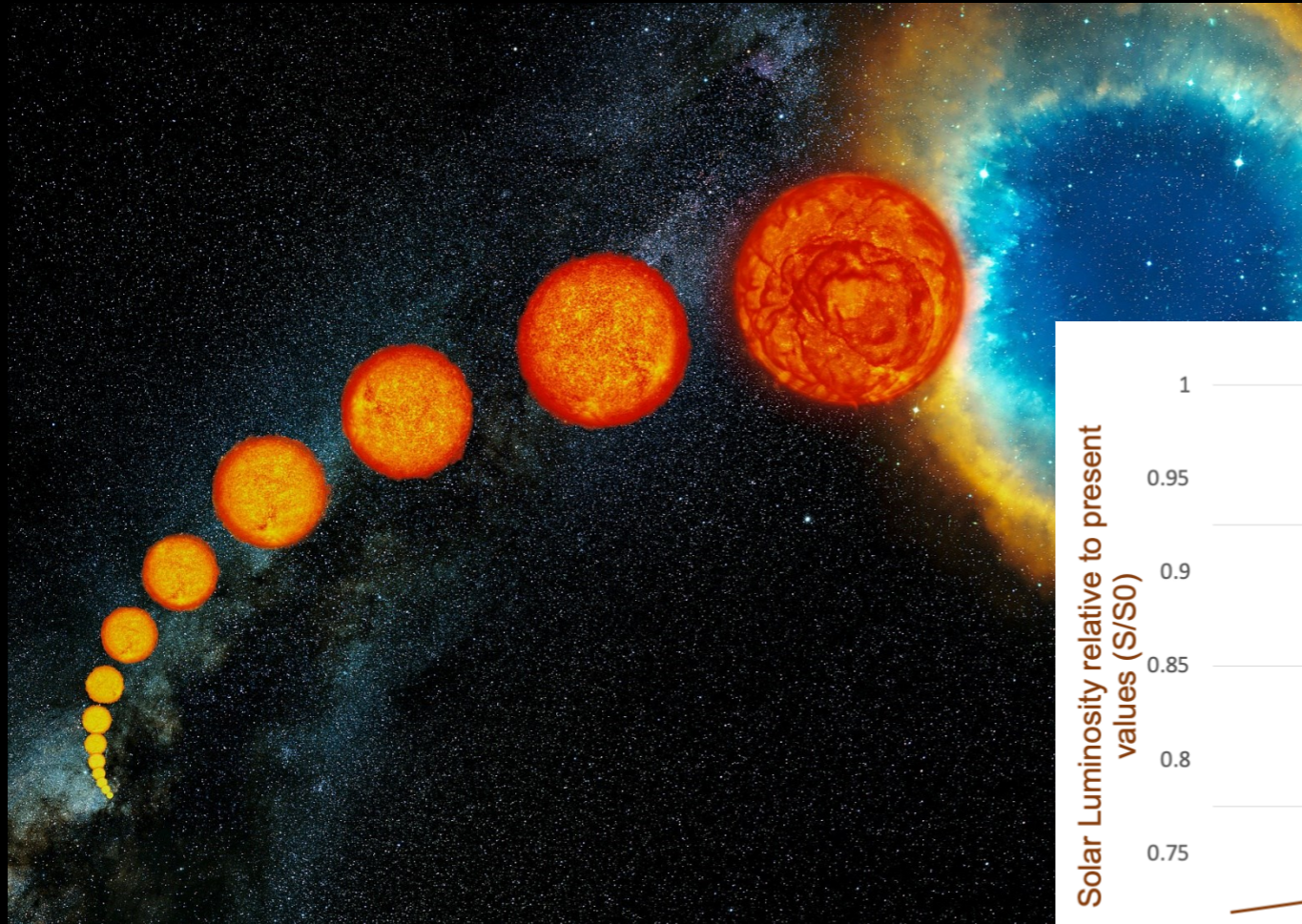
Climate buffer by the geological carbon cycle

Sequestration of CO₂ by carbonate burial plays fundamental role in regulating Earth climate through time

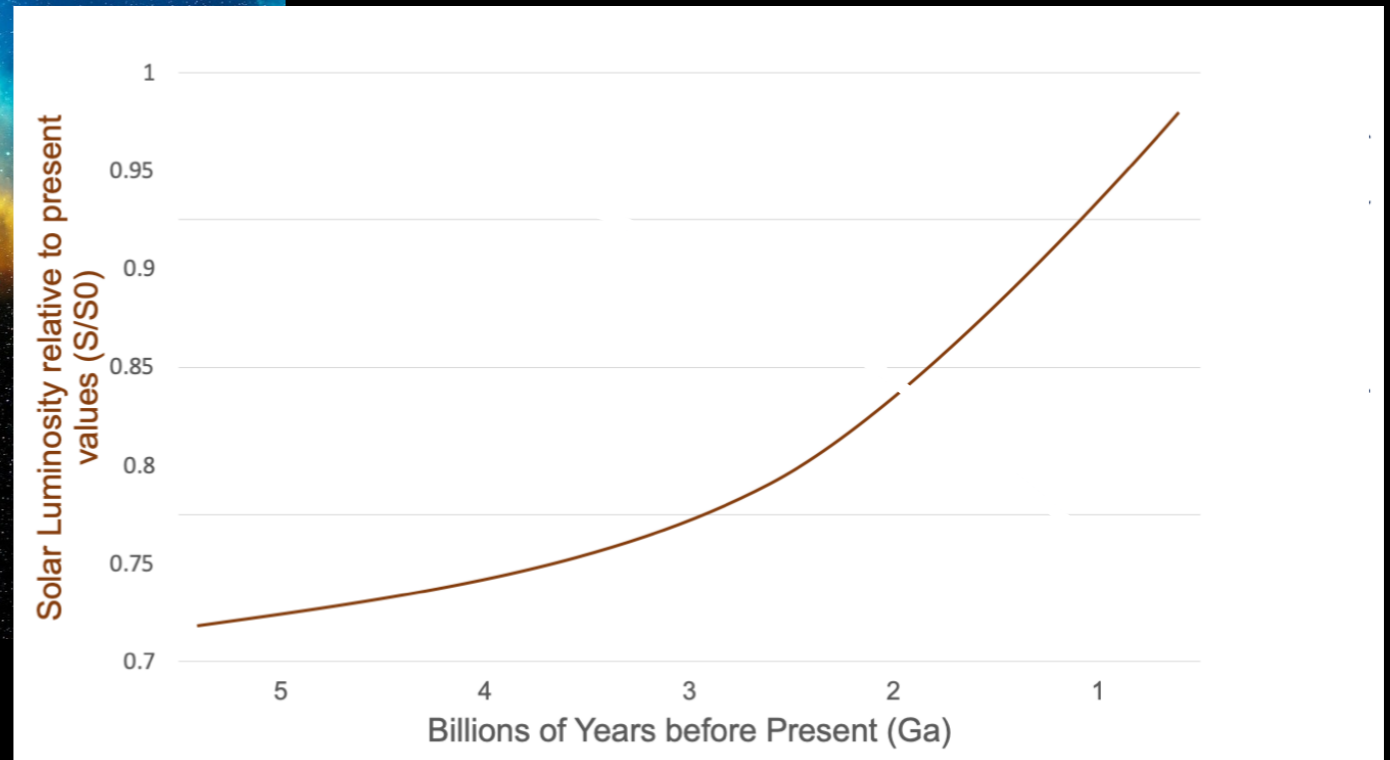


Climate buffer by the geological carbon cycle

The faint young Sun paradox

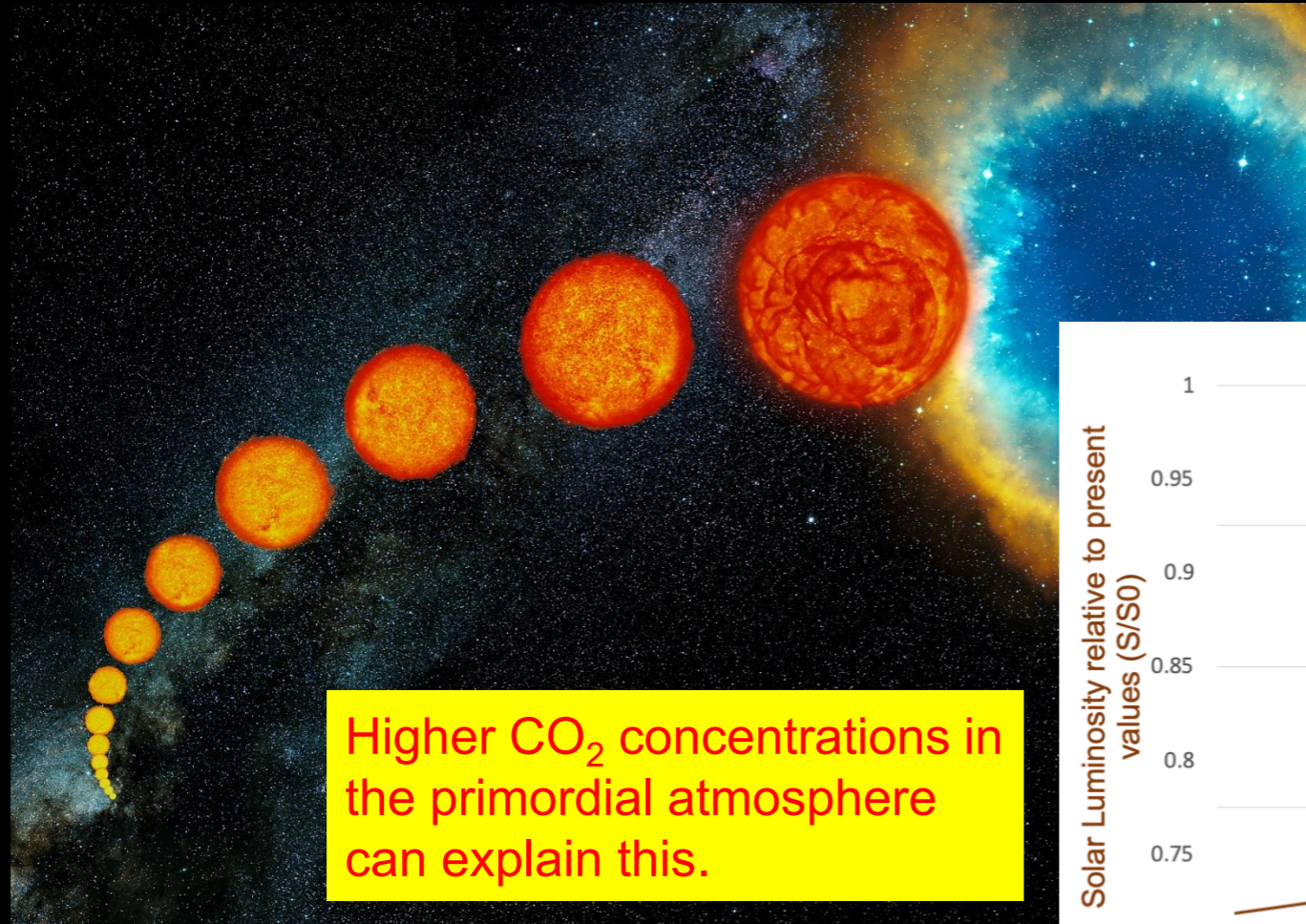


Astrophysical studies have shown that evolution of the Sun during its life cycle would have brought to a 30% increase in luminosity since the formation of Earth.

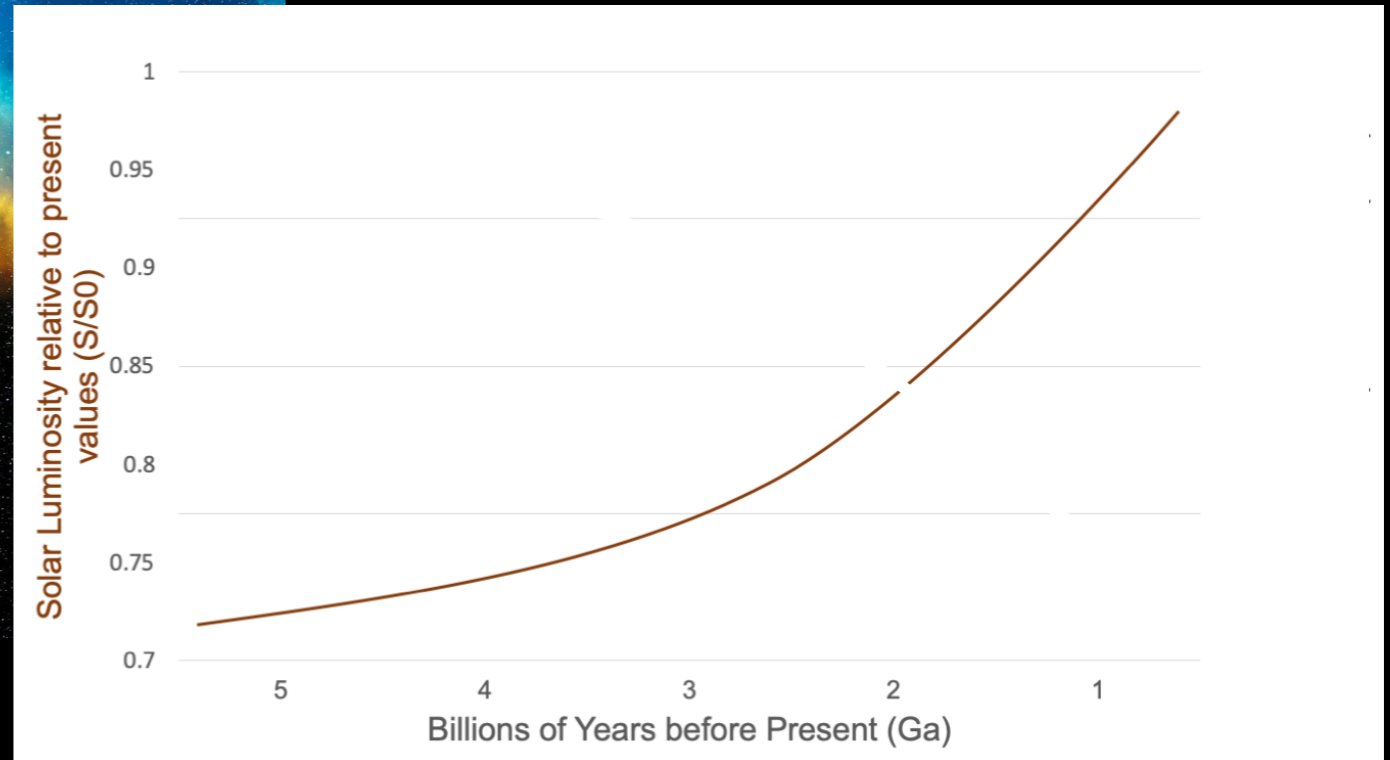


Climate buffer by the geological carbon cycle

The faint young Sun paradox

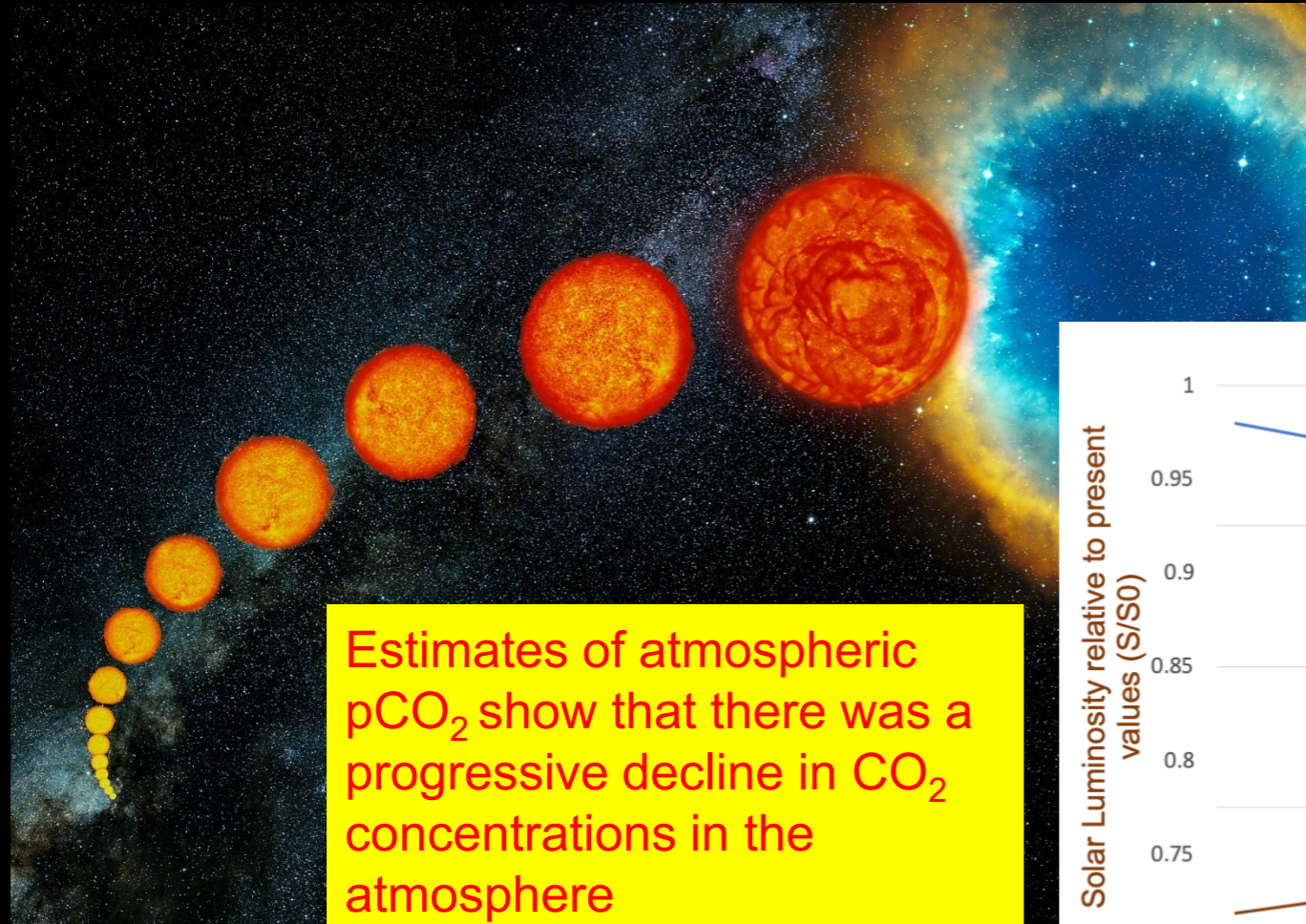


First problem: with a Sun 30% less luminous, Earth would have been completely frozen. Nevertheless there is evidence of liquid water (3.8 billion years old sedimentary rocks)

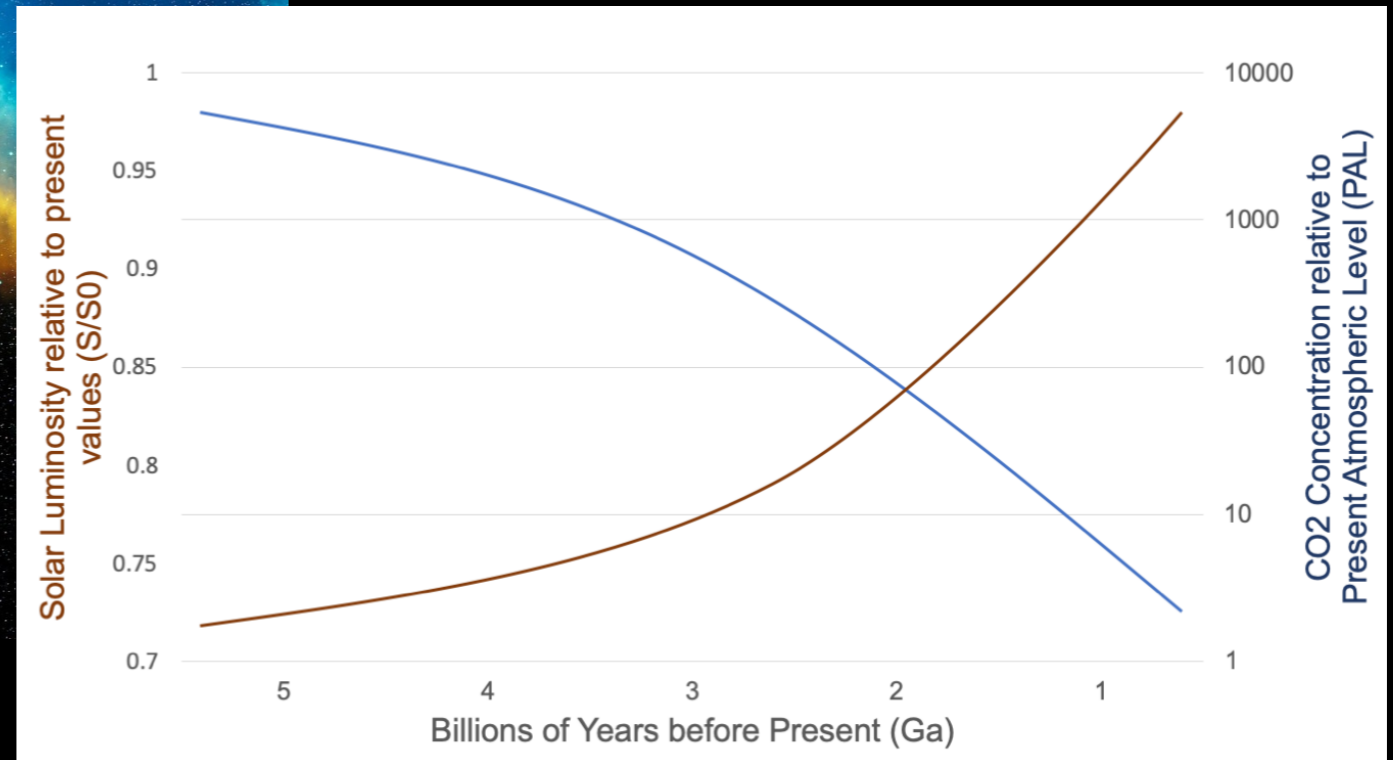


Climate buffer by the geological carbon cycle

The faint young Sun paradox



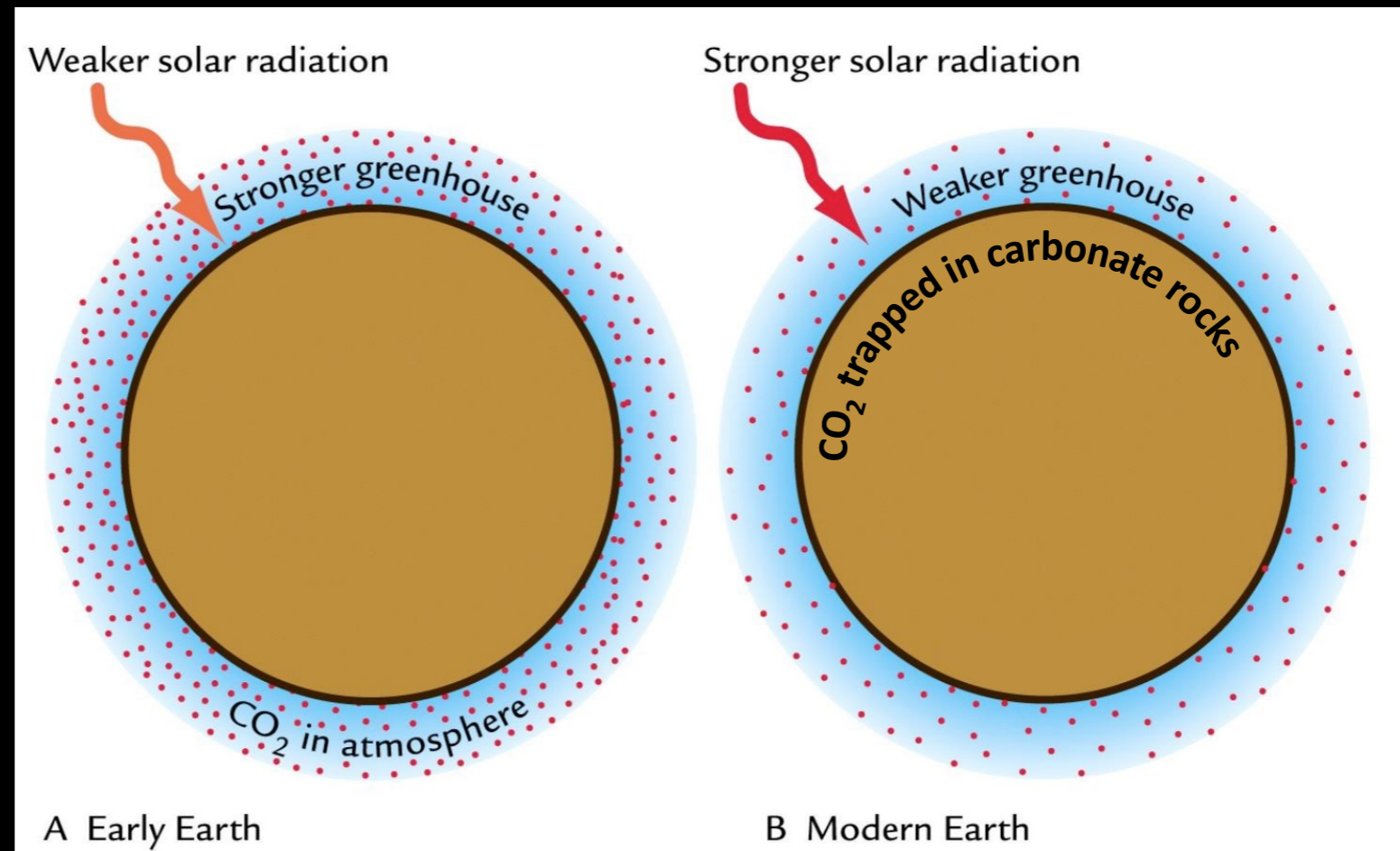
Second problem: how did temperature did not rise as it may be expected with the increase in luminosity?
If this had happened, life as we know may never had evolved.



Climate buffer by the geological carbon cycle

Current hypothesis is that the activation of the silicate/carbonate cycle, which made possible by the existence of liquid water on Earth, has balanced the increase in temperature that would have been caused by the progressive increase in Sun's luminescence by lowering CO_2 concentrations and therefore regulating the related greenhouse effect.

The precipitation of calcium carbonate for sure begun early in Earth history: oldest carbonate rocks date back to 3.5 Ga



Climate buffer by the geological carbon cycle

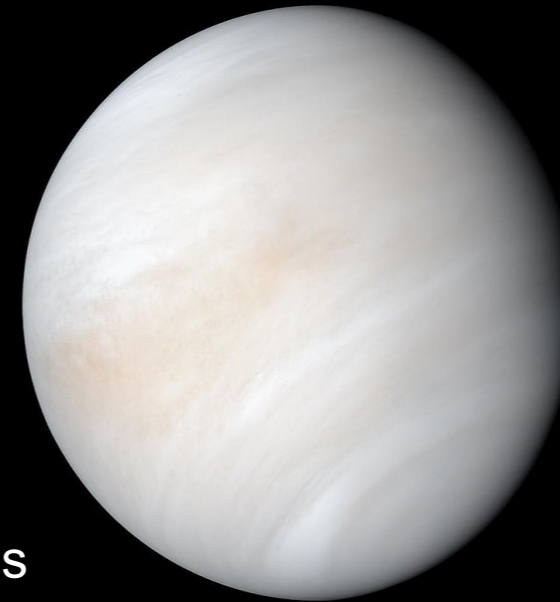
The **carbon cycle** is unique of planet Earth in the Solar System and exists because the distance from the Sun is such as liquid water is present and a C-cycle exists that is able to transfer back to the lithosphere part of the carbon that is emitted into the atmosphere by volcanoes. An example of planet where such mechanism is not working is Venus.



Earth

600 Gt carbon in the atmosphere
thanks to the C-cycle

Life as we know it possible



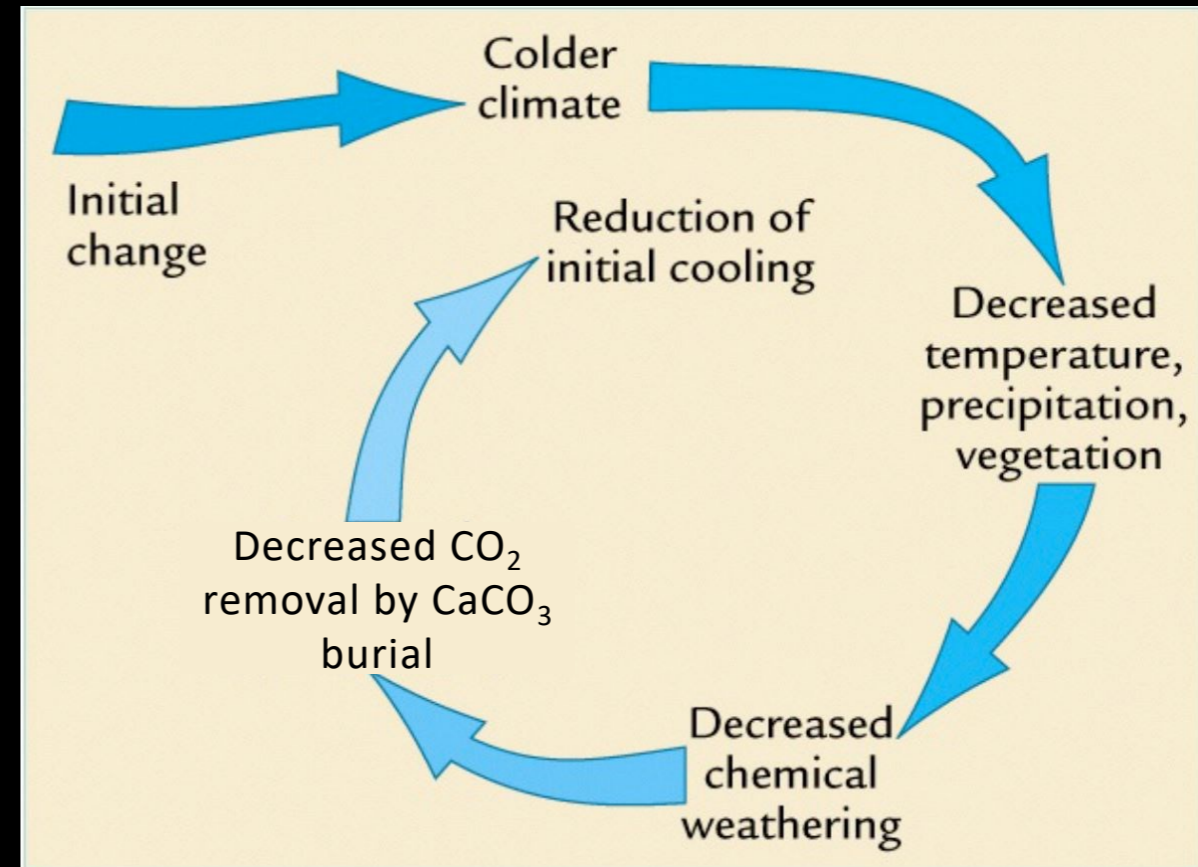
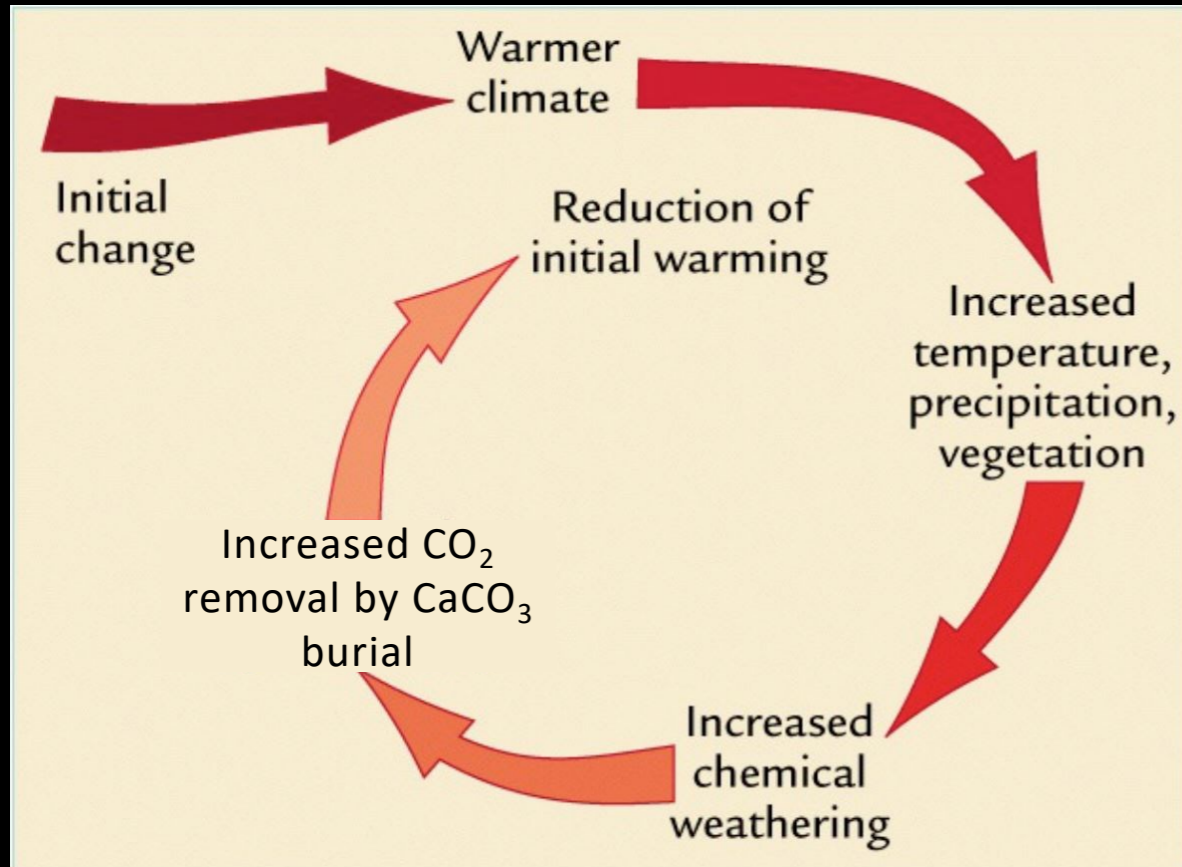
Venus

2×10^8 Gt carbon in the atmosphere
No C-cycle. All CO₂ emitted by volcanoes
in the atmosphere

Life as we know it not possible

Climate buffer by the geological carbon cycle

Negative feedback mechanism of the silicate/carbonate cycle.
Important effect of stabilization of Earth's climate on the long time scales

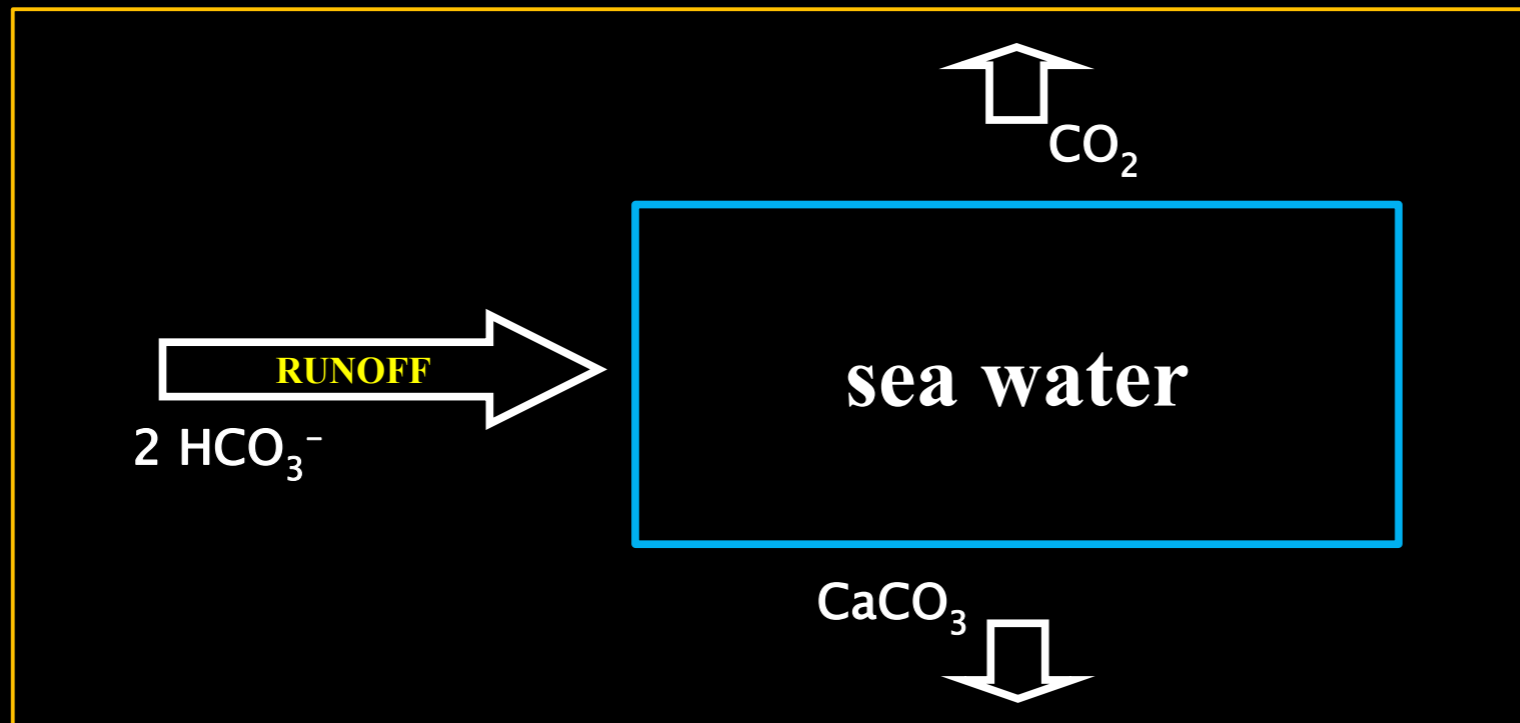


Thanks to the geological carbon cycle and the precipitation of carbonates in the oceans Earth's climate has a sort of thermostat that tends to buffer extreme oscillations in temperature!

The game is different on shorter time scales!

Let's look again at the precipitation reaction.

For each molecule of calcium carbonate that is precipitated, one molecule of carbon dioxide is released.



Precipitation releases CO₂, while dissolution consumes CO₂. Thus, in a closed system, **precipitation lowers the pH**, seawater becomes more acidic, and as a consequence precipitation stops.

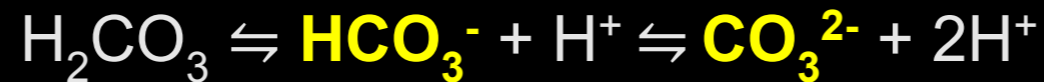
This process operates on time scales in the order of **thousand of years (10³)**

Carbon in the oceans

- normally we refer to inorganic carbon (**TIC**, total inorganic carbon)
- ...is present as **CO₂** in gaseous solution;
- Reacts with seawater to give carbonic acid:

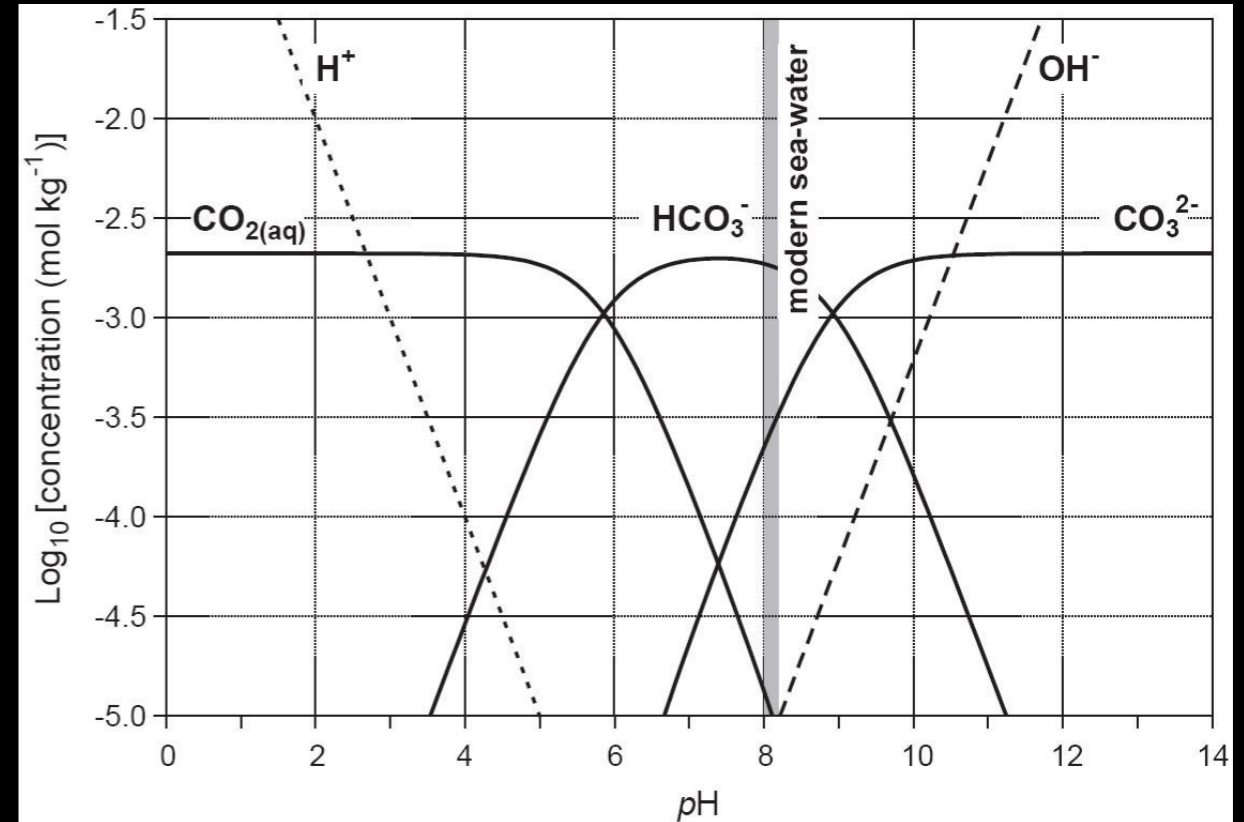


- Carbonic acid dissociates:

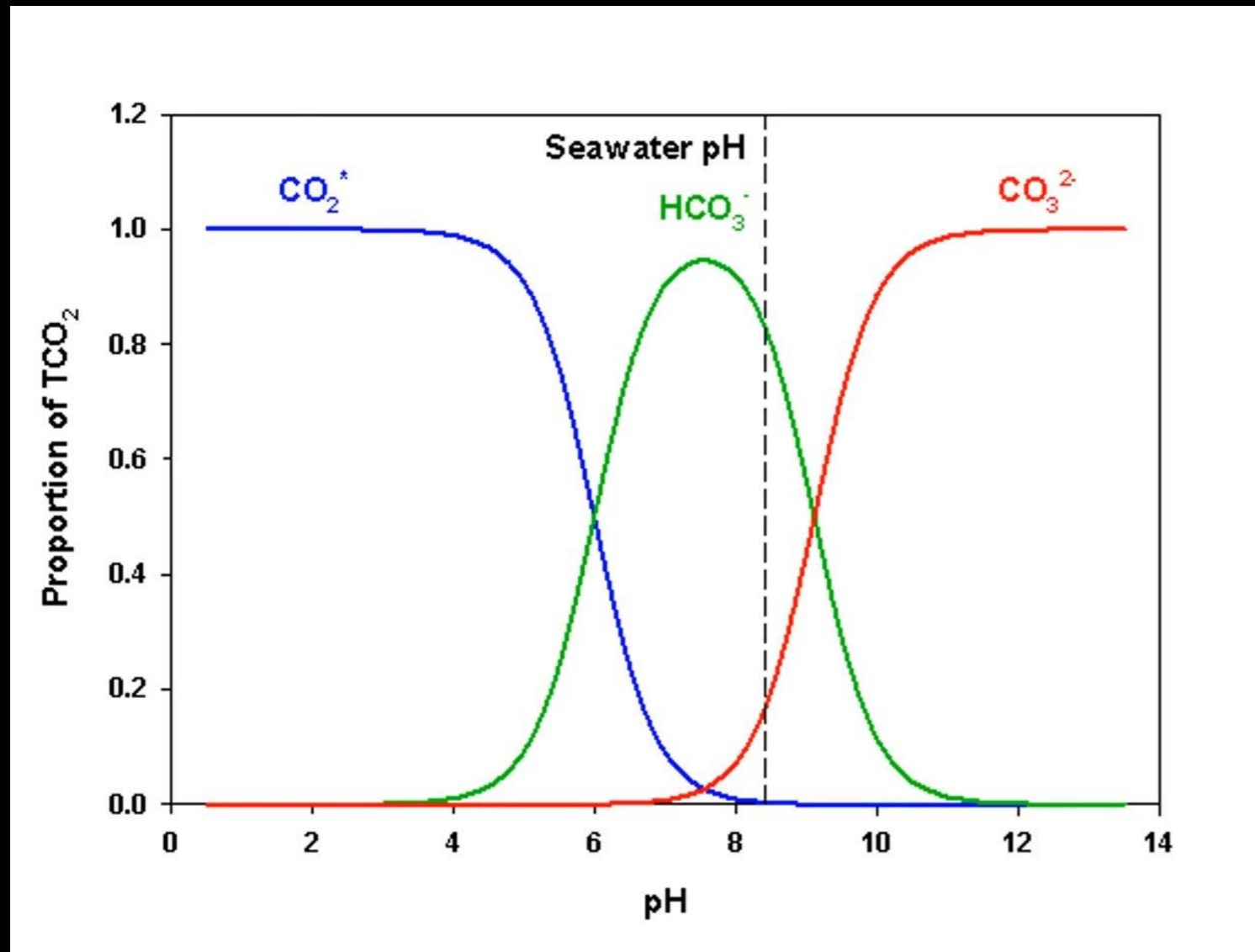


The form in which inorganic carbon is in the water depends on pH.
In present oceans, it is mostly HCO_3^- .

From Ridgwell and Zeebe, 2005.
Note that: (1) the higher the pH, the higher the concentration of carbonate ions; (2) modern seawater is far from neutral and is instead frankly alkaline.



Carbon in the oceans



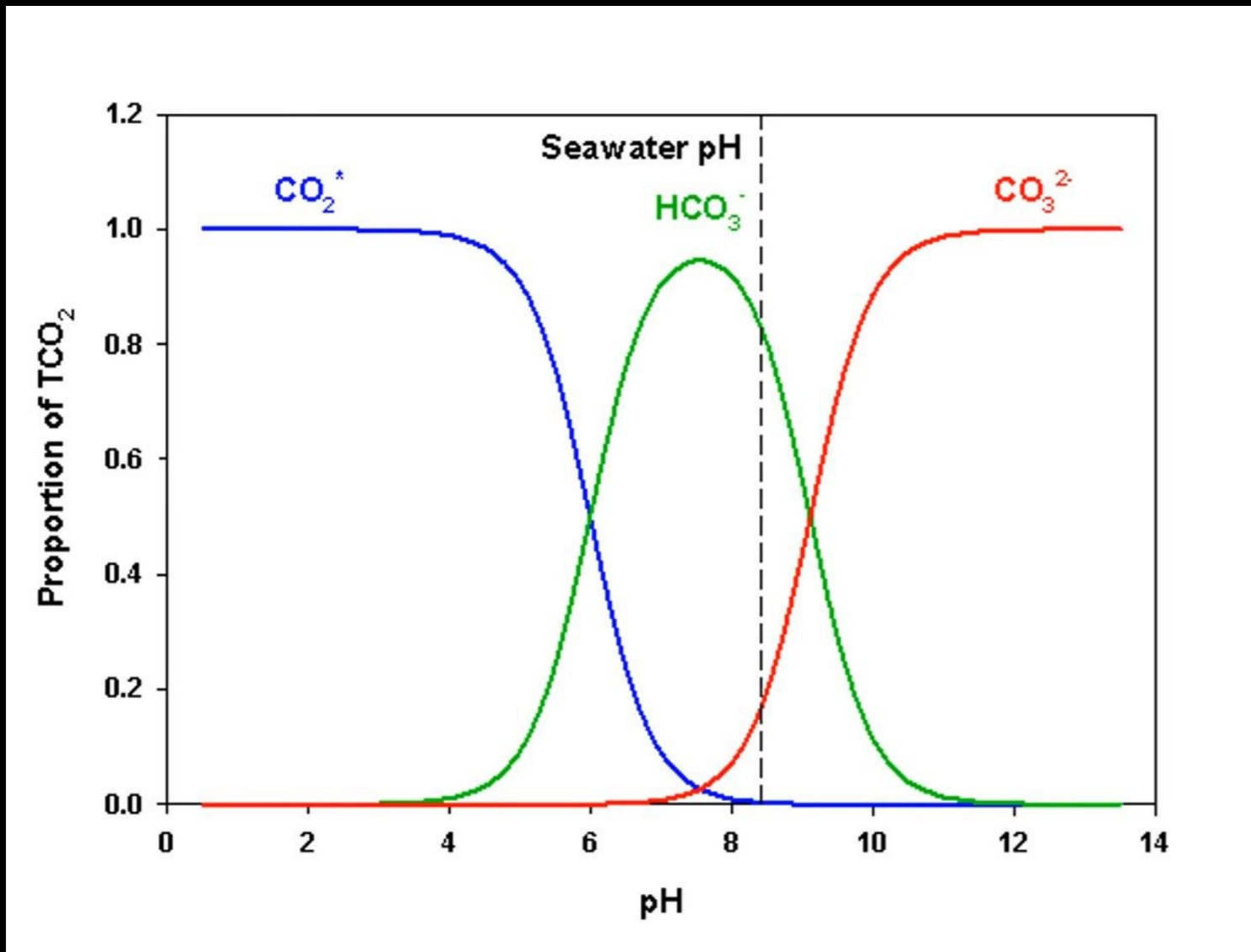
Partitioning of carbon species in seawater in function of pH

An important feature of the **carbonate system in seawater** is that it is a **buffering system**.

This means that the equilibrium of the reactions that govern the proportions of the various species in which carbon is dissolved in water tends to resist to rapid variations in pH.

This phenomenon contributes to make the marine environment stable and stability is important for life and its evolution.

Carbon in the oceans



Partitioning of carbon species in seawater in function of pH

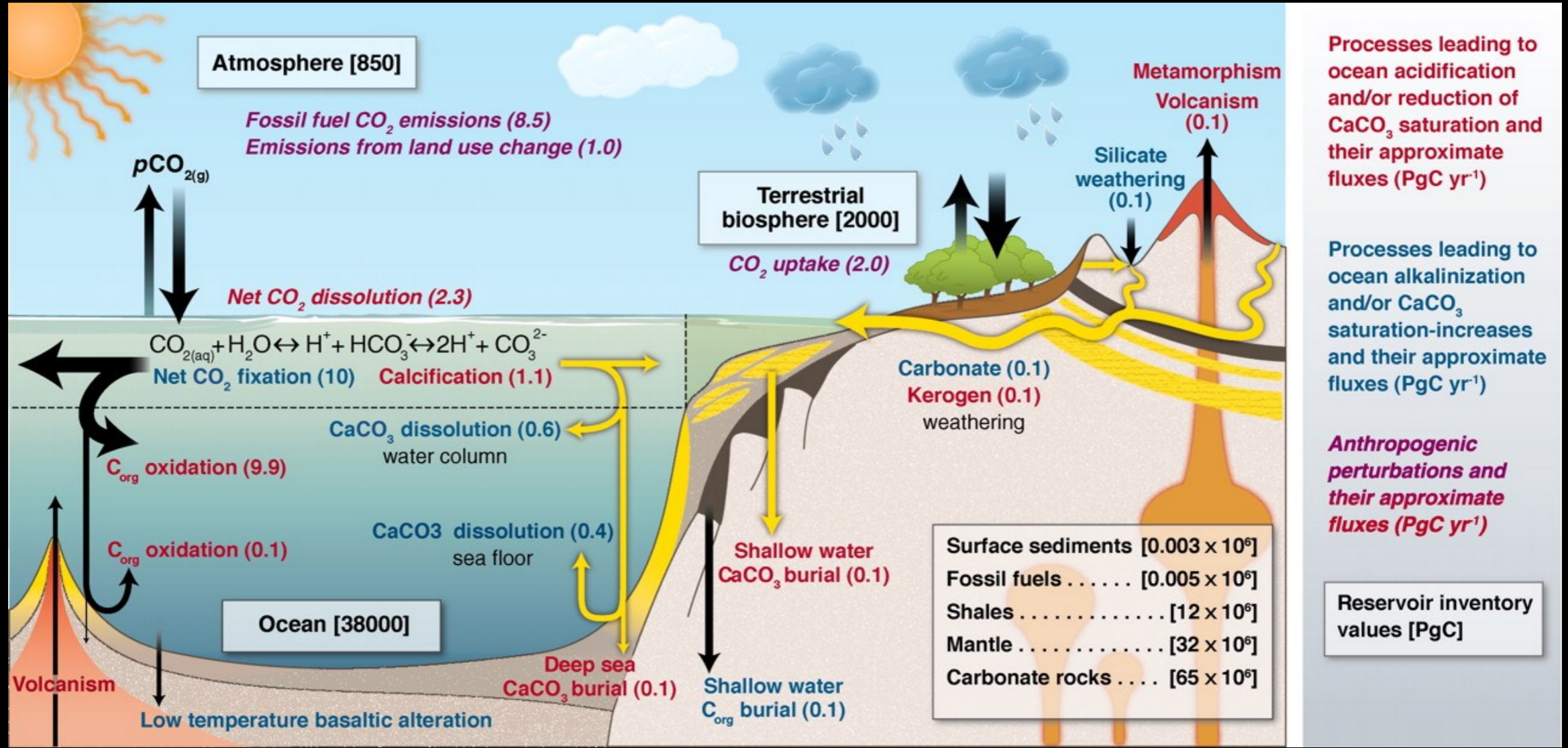
If pCO₂ in seawater increases, free hydrogen (H⁺) concentration increases, thus lowering pH (this is called **acidification**).

However, carbonate in seawater, if pH decreases, tends to dissolve, forming free calcium (Ca²⁺) ions and free bicarbonate (HCO₃⁻) ions .

The free hydrogen ions are therefore consumed resulting in decreased hydrogen ion activity.

This creates the buffering effect of carbonate system in seawater.

Carbon in the oceans



The carbon cycling in the oceans according to Hönisch et al., 2012.

1 Pg = 10^{12} Kg

Carbonates vs clastics



VS



Carbonates vs clastics

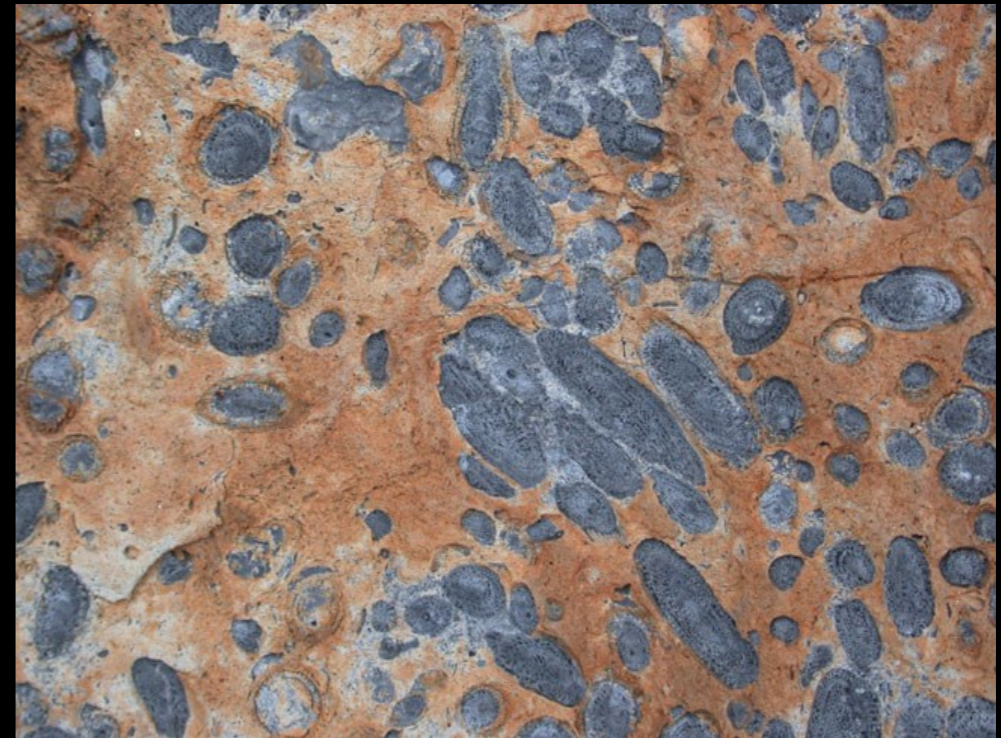


300 million year old ripples next to 300 minute old ripples. Photo credits [Ian Kane](#)

Carbonates vs clastics



Carbonate rock with bryozoan, echinoids and brachiopods



Carbonate rock with fusulinids

Carbonate rocks like clastic rocks derive from sediments, but they are fundamentally different.

- Carbonates are often formed with the **mediation of living organisms** (up to 90-95% grains are biogenic in origin)
- Carbonate precipitation is a **chemical reaction**.

Carbonates vs clastics

Carbonate sediments are formed via precipitation of carbonate minerals (a chemical reaction) from a solution, usually seawater. Precipitation may be mediated by living organisms.



Epiclastic sediments are formed via weathering and/or erosion of a pre-existing rock, transportation and deposition. These are mostly physical processes.



Carbonates vs clastics

Three main consequences:

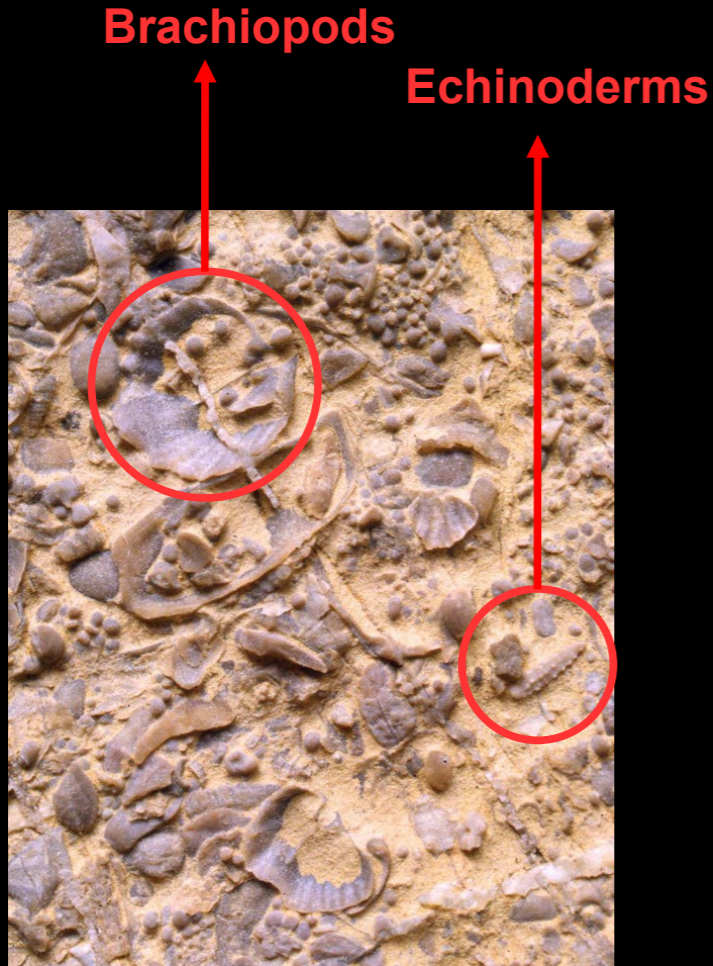
- Sediment do not come from somewhere in the hinterland: in carbonate systems, **sediments are produced in situ***;
- Carbonate sediments are often subject to **early lithification**: carbonate cement may even form directly from seawater.
- When **life** is involved things can get fairly complicated as **evolution** is part of the game.

*) “Carbonates are born, not made”
(James, 1983)

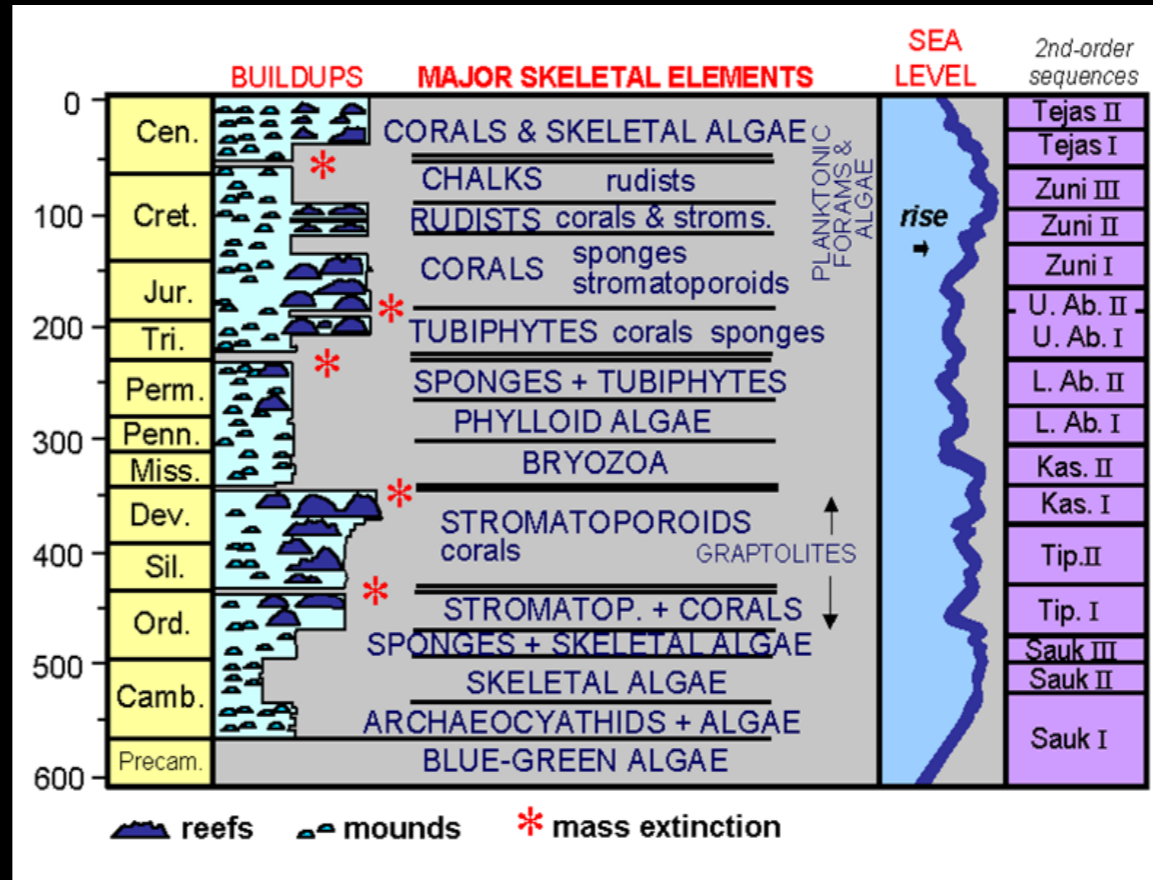


Carbonates: the biological factor

- “Carbonates are born, not made”
(James, 1979)
- Evolution is part of the game



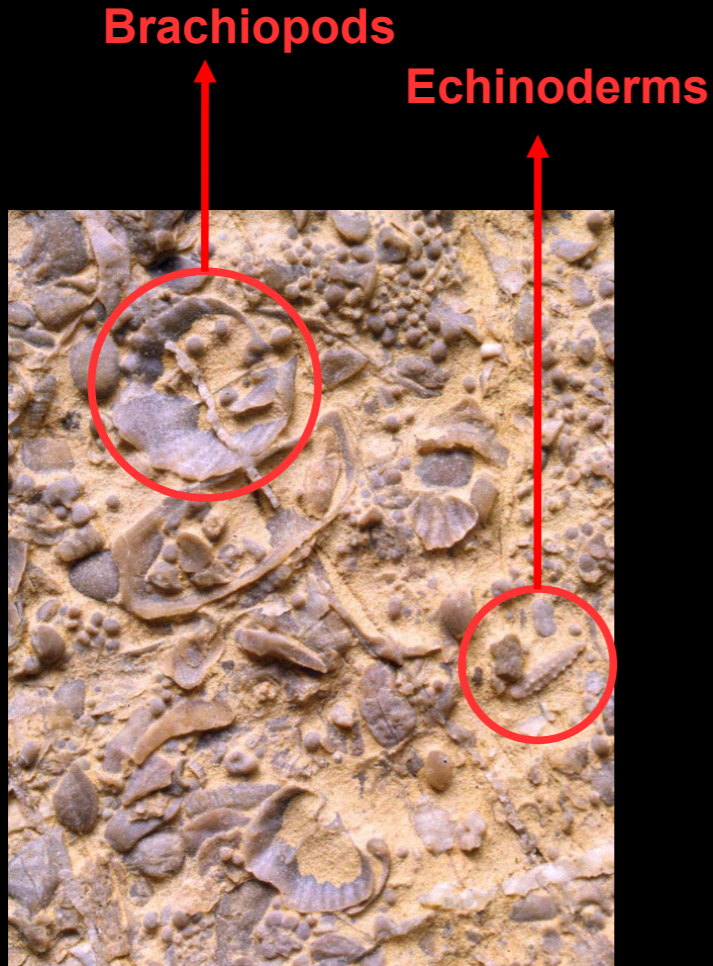
Carbonate rocks may contain skeletal grains



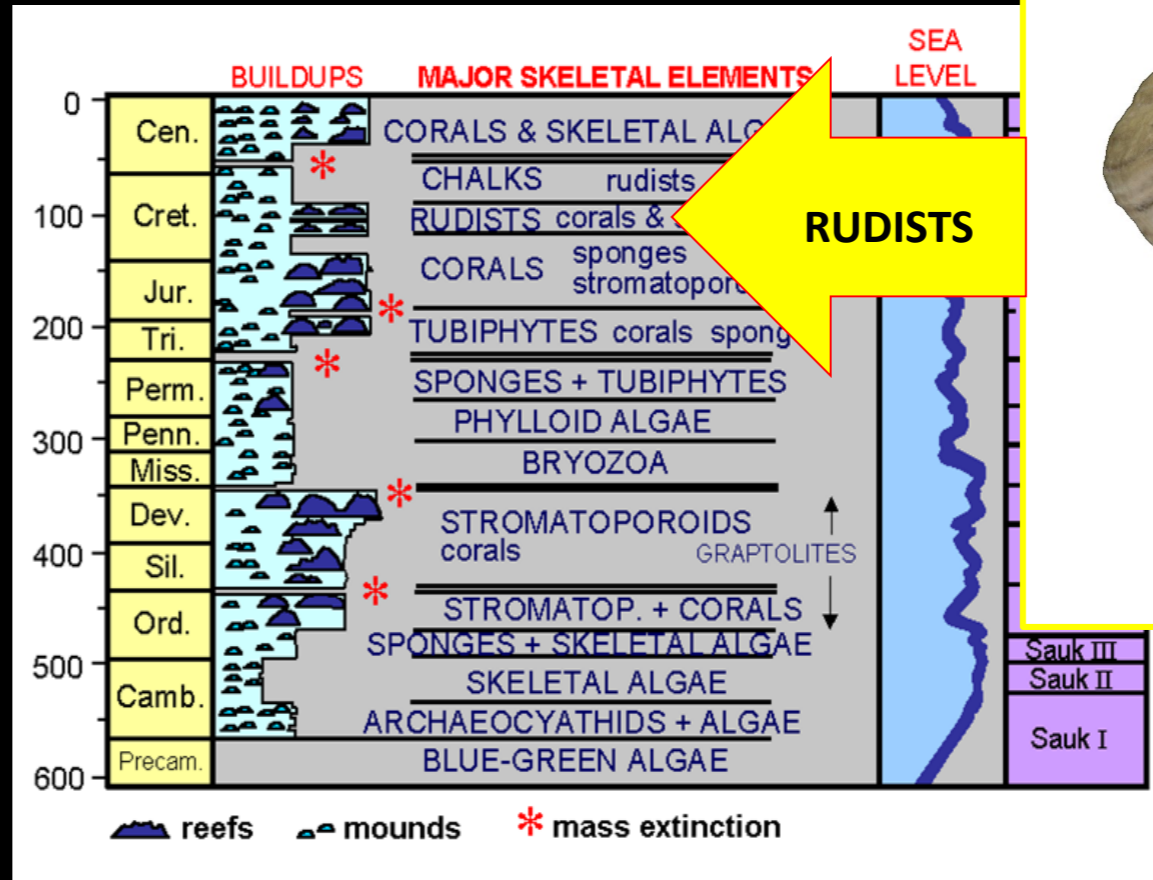
Reef-building organisms changed through geological time. “The play has remained the same, only the players have changed” says Bob. Redrawn from James, 1983.

Carbonates: the biological factor

- “Carbonates are born, not made”
(James, 1983)
- Evolution is part of the game



Carbonate rocks may contain skeletal grains

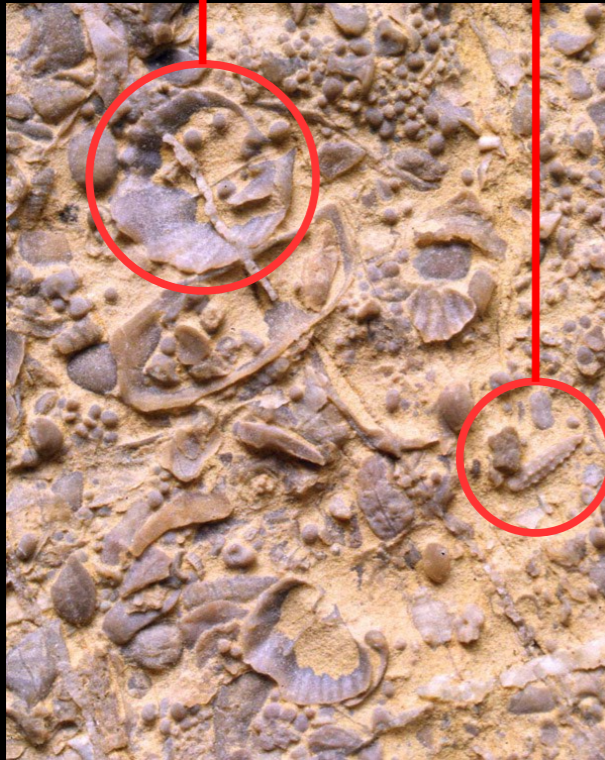


Reef-building organisms changed through geological time. “The play has remained the same, only the players have changed” says Bob. Redrawn from James, 1983.

Carbonates: the biological factor

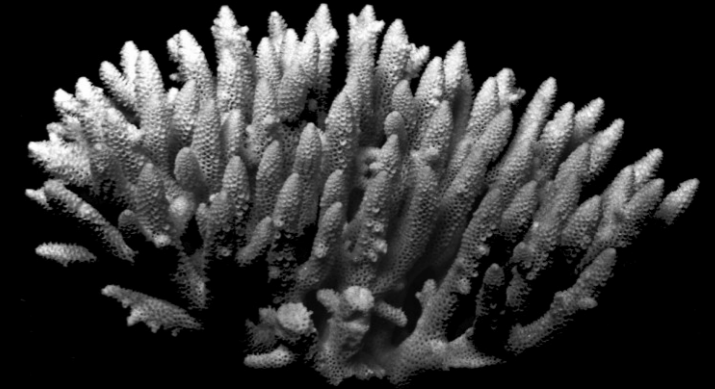
Brachiopods

Echinoderms



Carbonate rocks may contain skeletal grains

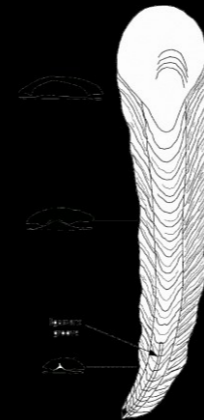
Reef-building organisms with carbonate shells or skeletons were there since the Precambrian.
ecological preferences may have changed.



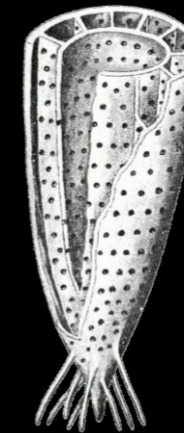
Scleractinian coral
Cenozoic to present



Rudist
Cretaceous



Lithiotis sp.
Early Jurassic

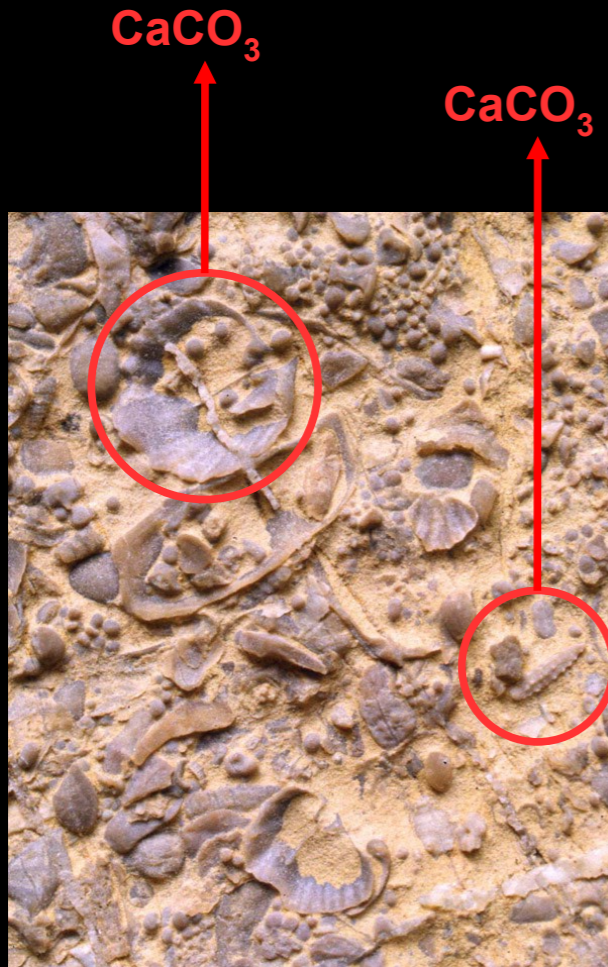


Archaeocyatha
Cambrian



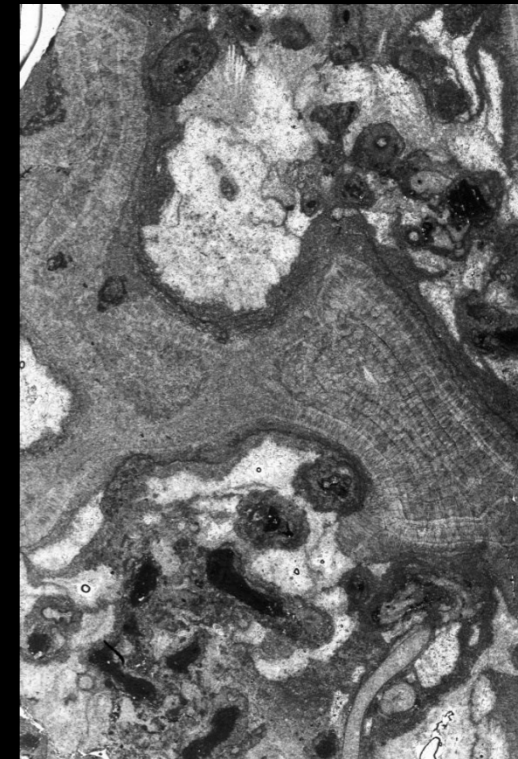
Stromatolite
Precambrian

Carbonates: the chemical factor



Carbonate rocks are made of carbonate minerals

All components of a carbonate rock are the product of a chemical reaction (precipitation of a carbonate mineral from seawater).



A cementstone is a carbonate rock which framework is substained by marine cement

Take home messages from this class

- The study of carbonates involves notions of chemistry and biology
- The precipitation of carbonates and the formation of carbonate rocks are a fundamental part of the global carbon cycle
- Carbonates are born, not made
- Never forget the precipitation-dissolution reaction!

