# Carbonate Sedimentology



- 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

- This course grants 6 credits organized in:
  - 24 hours in class or lab
  - 36 hours in the field

Field work deliverables

 Lectures will be on Wednesday (11am - 13pm room "C" bld. "C") and Thursday (2pm – 4pm, room "C" bld. "O") of the San Giovanni campus

50%

50%

- Field excursions (dates to be scheduled, ideally in April and June):
  - one 1-day excursion in the Karst area.
  - one 3 to 4-days excursion to the Latemar.

# How you'll be evaluated:

•	Oral examination	

# Course organization calendar

CLASSES			
	TOPIC	Date (2025)	
1	Introduction	March 5	
2	Precipitation of carbonates	March 6	
3	Carbonate factories + SEMINAR	March 12	
4	Carb. Factories continuation + T-type (1)	March 13	
5	T-type (2)	March 19	
6	C-type	March 20	
7	M-type	March 26	
8	Deep water carbonates	March 27	
9	Petrography of carbonates (1)	April 2	
10	Petrography of carbonates (2)	April 3	
11	Carbonate platform geometries	April 9	
12	Sequence Stratigraphy of carbonates	April 10	

LAB and EXCURSIONS				
TOPIC				
Microscopy lab	April 2			
Microscopy lab	April 3			
1-day excursion Karst area	April or May			
3-days excursion Dolomites	June			

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

Changes are 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

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 Microfacies of carbonate rocks - Flügel, Springer-Verlag, Berlin-Heidelberg (Germany), 2004 (and subsequent editions)

#### How can you find me?

- e-mail: mfranceschi@units.it
- In room 217 of Building "Q" (or drop me a e-mail and get an appointment)

#### What are carbonates?

- Carbonate in chemistry is salt of carbonic acid (H<sub>2</sub>CO<sub>3</sub>)
- 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 posses 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





Continuous carbonate rocks



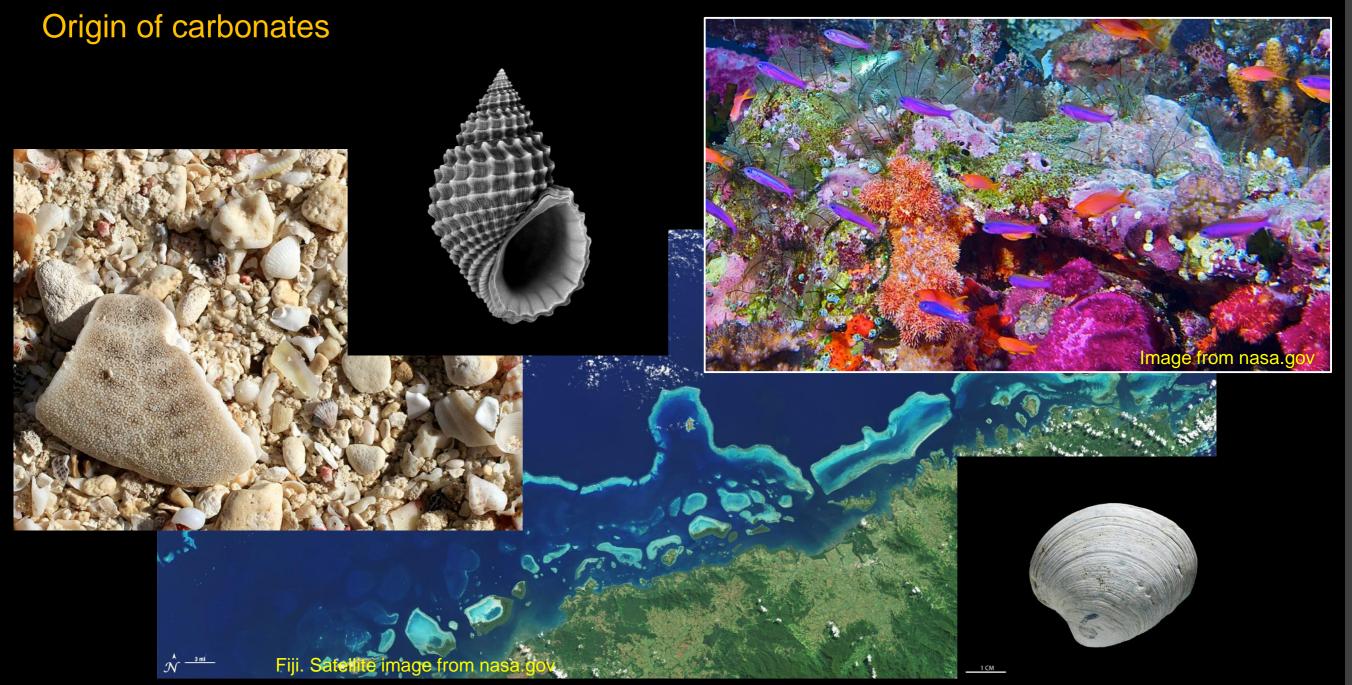
Discontinuous carbonate rocks



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.

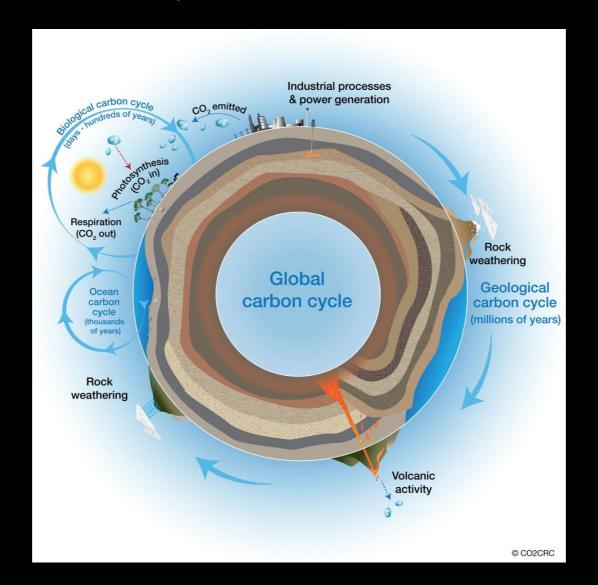
Large volumes of carbonate rocks also exist in the subsurface and can host important hydrocarbon and groundwater reservoirs.



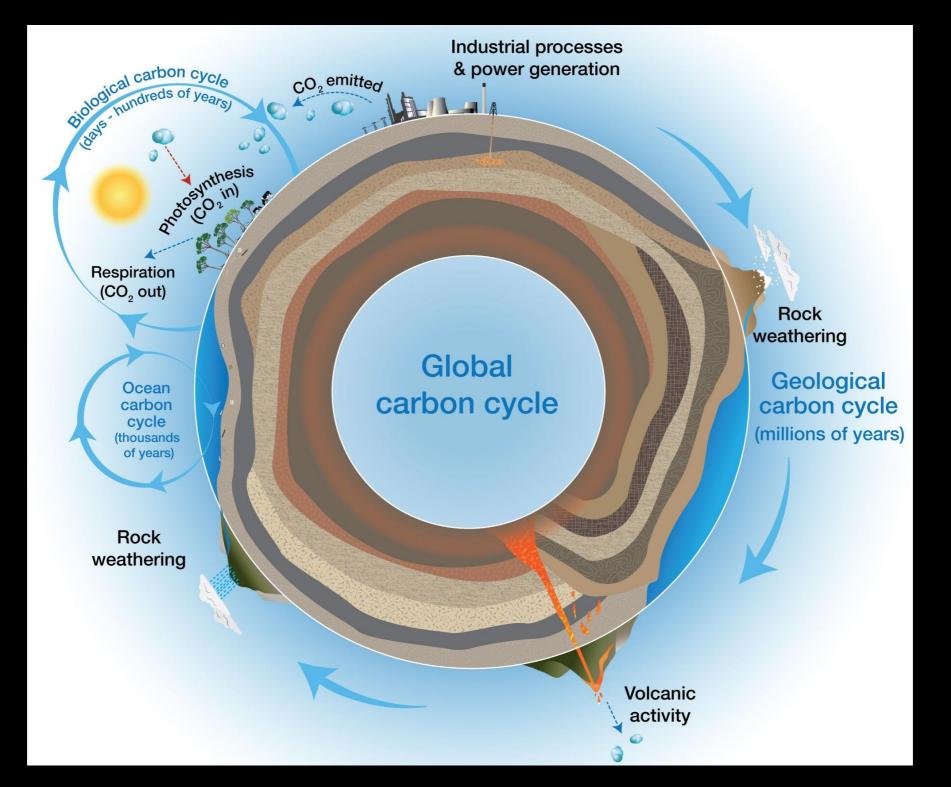
#### The carbon cycle

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 Ccycle on timescales ranging from  $10^3$  –  $10^6$  yr.



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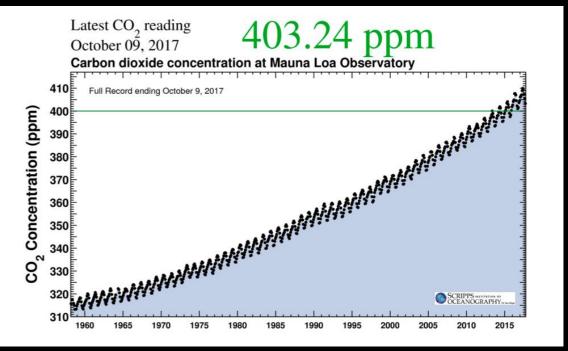
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The partial pressure, or concentration, of CO<sub>2</sub> in the surface water of the oceans and in the atmosphere are roughly in equilibrium on a short (weeks) time scale.

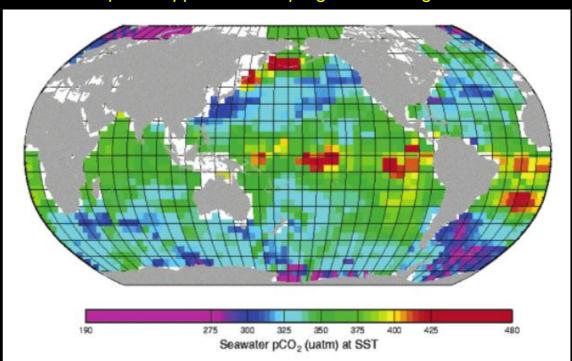
$$pCO_2 \equiv [CO_2]$$

The concentration of Carbon Dioxide in the atmosphere is rising, and is now > 400 ppm. Hydrolysis of silicates consumes excess  $CO_2$  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 pCO<sub>2</sub> of oceans' surface waters (from Millero, 2007, Chem. Rev., 107:308-341).

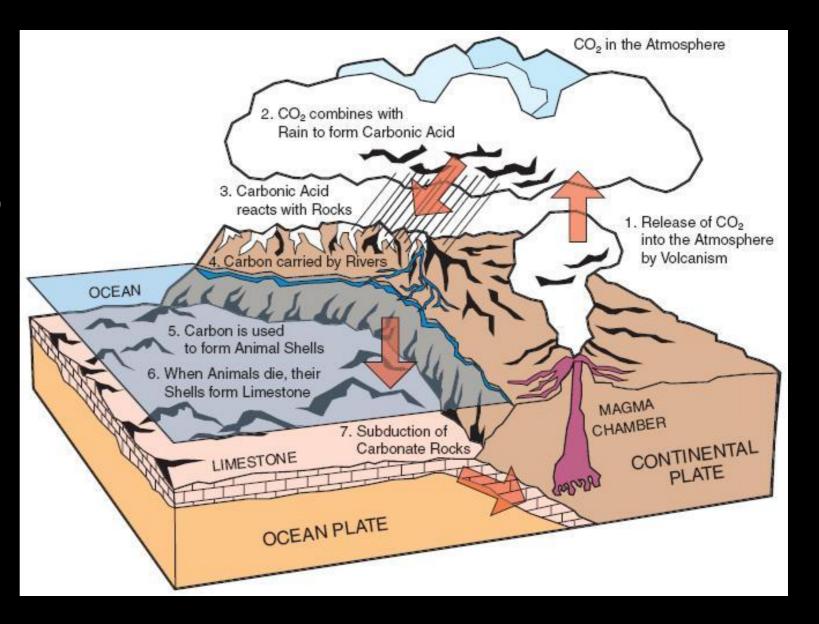


https://scripps.ucsd.edu/programs/keelingcurve/



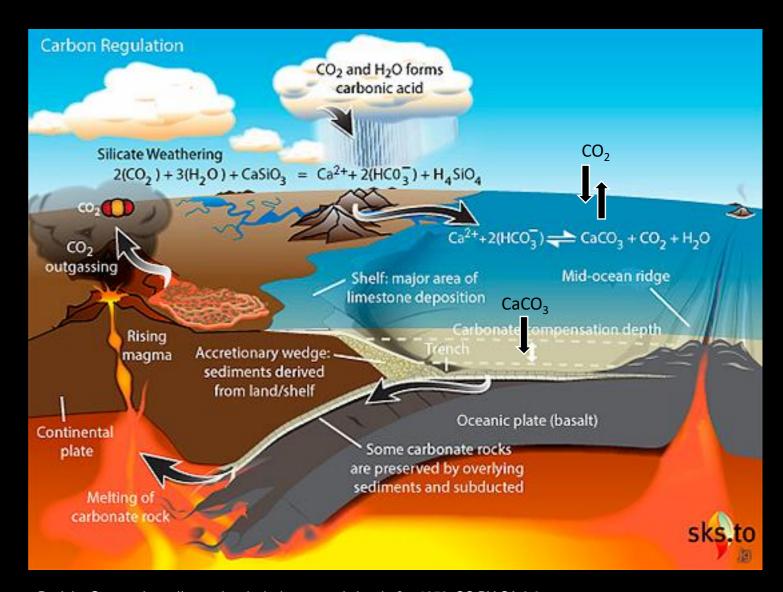
With the term inorganic carbon we refer to the carbon that is found primarily in compounds such as carbon dioxide  $(CO_2)$ , carbonic acid  $(H_2CO_3)$ , bicarbonate  $(HCO_3^{-1})$ , and carbonate  $(CO_3^{-2})$ 

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



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



By John Garrett - https://www.skepticalscience.com/print.php?n=1959, CC BY-SA 3.0, https://commons.wikimedia.org/w/index.php?curid=74327875

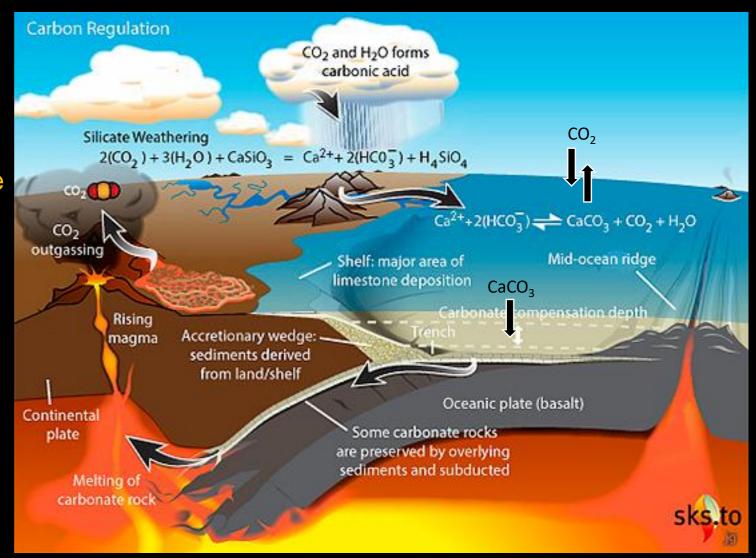
Carbon enters seawater in two ways:

- As CO<sub>2</sub> from the atmosphere
- As carbonate (CO<sub>3</sub><sup>2</sup>-) and hydrogen carbonate (HCO<sub>3</sub><sup>-</sup>) ions with runoff (e.g., rivers)

Carbon leaves seawater as calcium carbonate (CaCO<sub>3</sub>) in sediments

When carbonate rocks are subducted the stored carbon is ultimately released as volcanic CO<sub>2</sub>

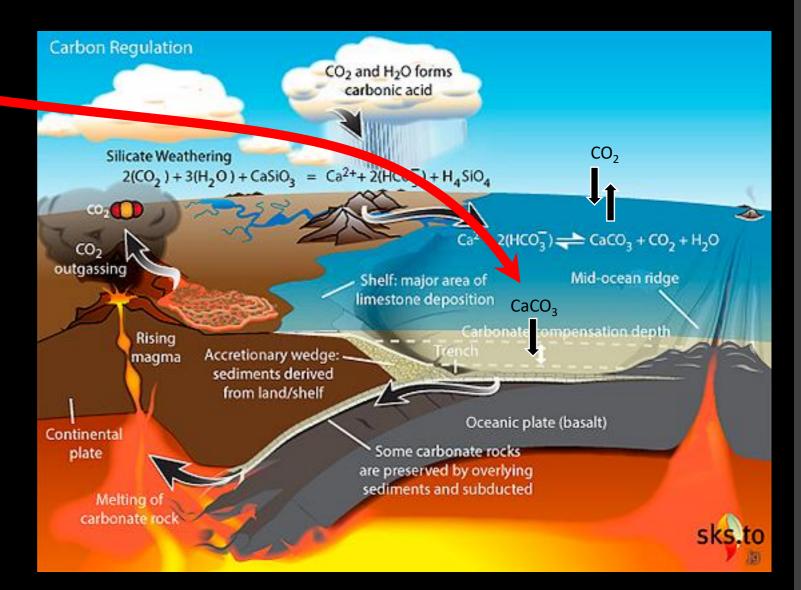
CO<sub>2</sub> then participates to silicate weathering (e.g. anortite weathers in kaolinite) and is transferred to oceans as carbonate ions through runoff... and the loops starts again



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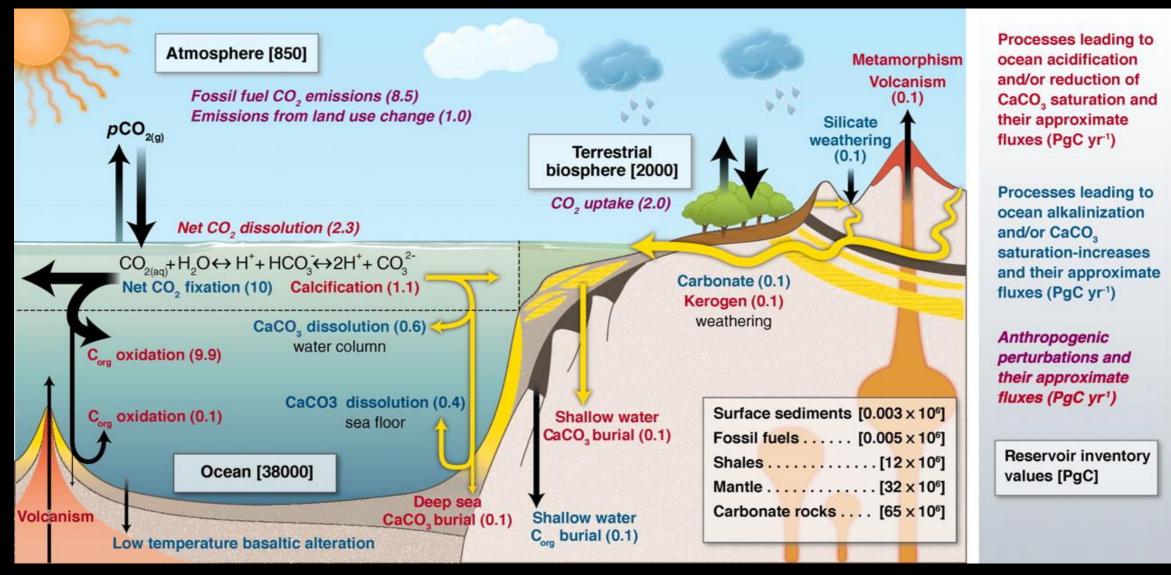
The majority of carbonates precipitate in the oceans and form carbonate sediments and ultimately, through lithification, become carbonate rocks

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).



By John Garrett - https://www.skepticalscience.com/print.php?n=1959, CC BY-SA 3.0, https://commons.wikimedia.org/w/index.php?curid=74327875

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



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

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# The carbonate dissolution – precipitation equilibrium reaction

DISSOLUTION

$$Ca^{2+} + 2HCO_{3}^{-} \hookrightarrow CaCO_{3} + CO_{2} + H_{2}O$$

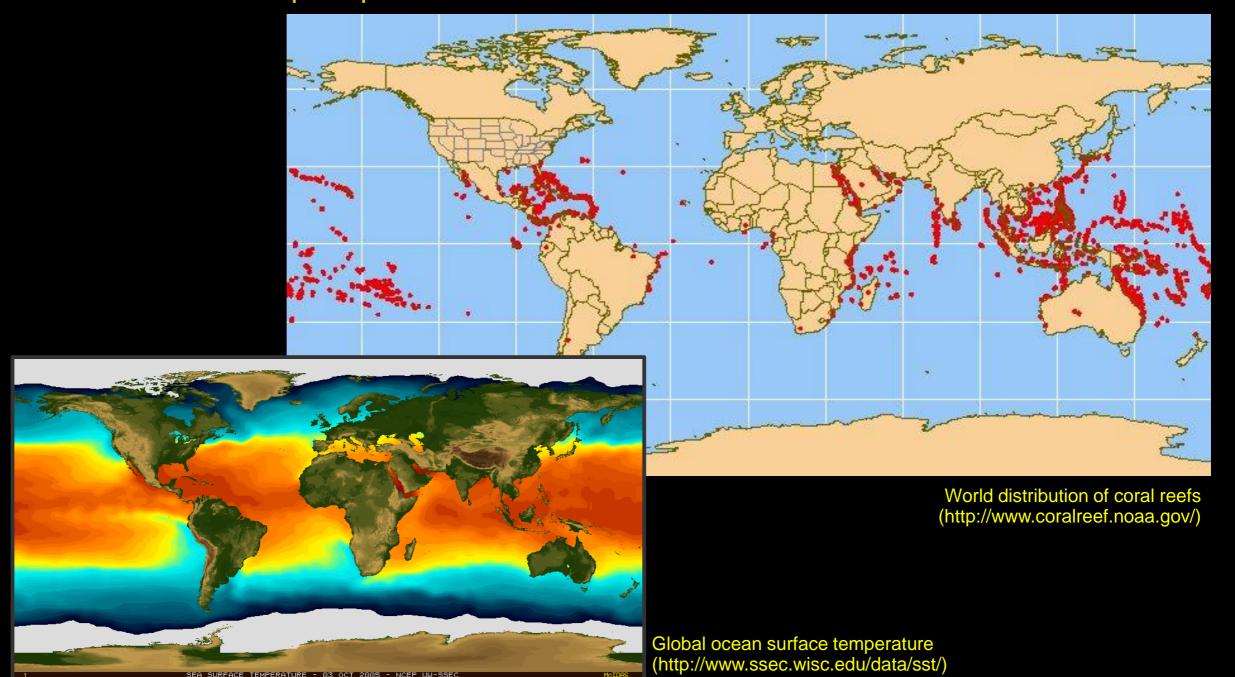
PRECIPITATION

T, pH,  $\Omega$ 

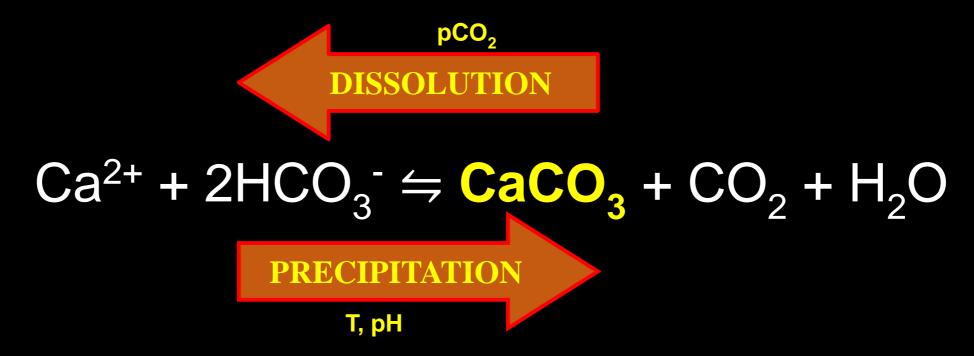
The dissolution-precipitation reaction is an equilibrium reaction which equilibrium constant changes in function of (mostly):

- T: Carbonate is precipitated as temperature rises.
- pH: Carbonate is precipitated as pH rises.
- pCO<sub>2</sub>: Carbonate is dissolved as pCO<sub>2</sub> rises.
- Ω: carbonate precipitation increases is saturation state with respect to carbonate increases.

# Controls on carbonate precipitation



#### Controls on carbonate precipitation



pCO2, T and pH influence the reaction. Furthermore, a major controller is seawater saturation state with respect to carbonate  $(\Omega)$ 

#### **ION CONCENTRATIONS**

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

The saturation state of seawater with respect to carbonate,  $\Omega$ , indicates whether sea water tends to precipitate CaCO<sub>3</sub> ( $\Omega$  >1; supersaturation)

or to dissolve  $CaCO_3$  ( $\Omega$  <1; undersaturation).

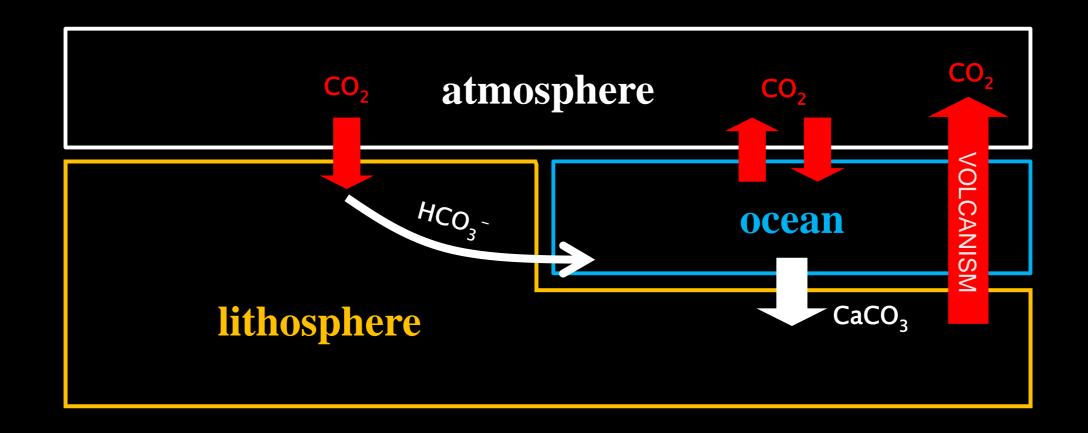
REACTION CONSTANT

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

$$CaAl_2Si_2O_8 + 3H_2O + 2CO_2 \rightarrow Ca^{++} + 2HCO_3^- + Al_2Si_2O_5(OH)_4$$
 Hydrolisis of silicates

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

Carbonate precipitation



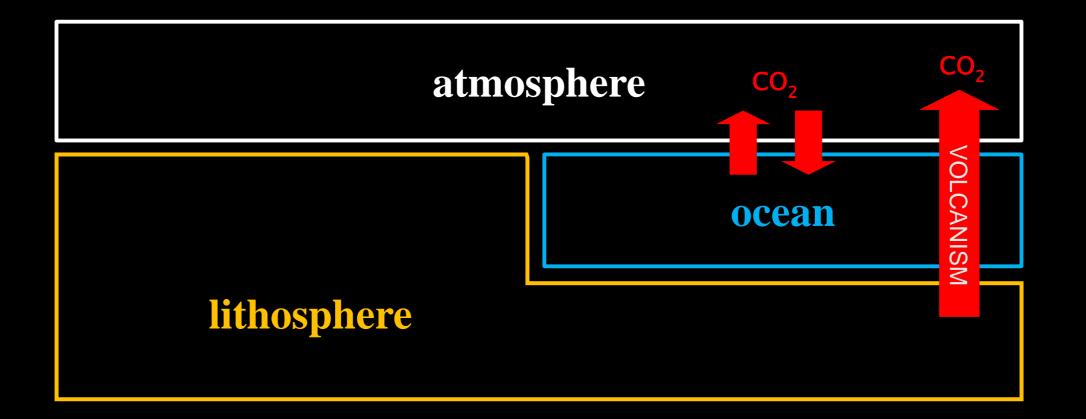
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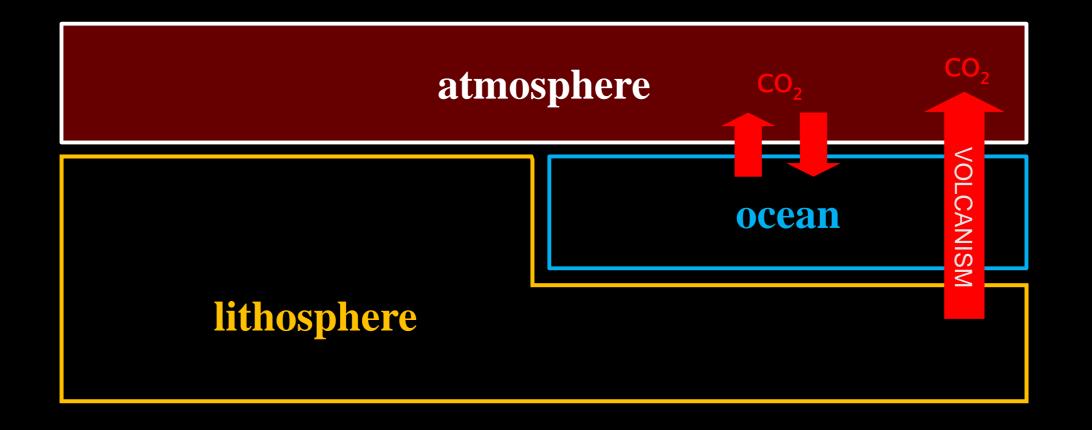
Carbonate precipitation

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<sub>2</sub> in the atmosphere and transfers it to the lithosphere.

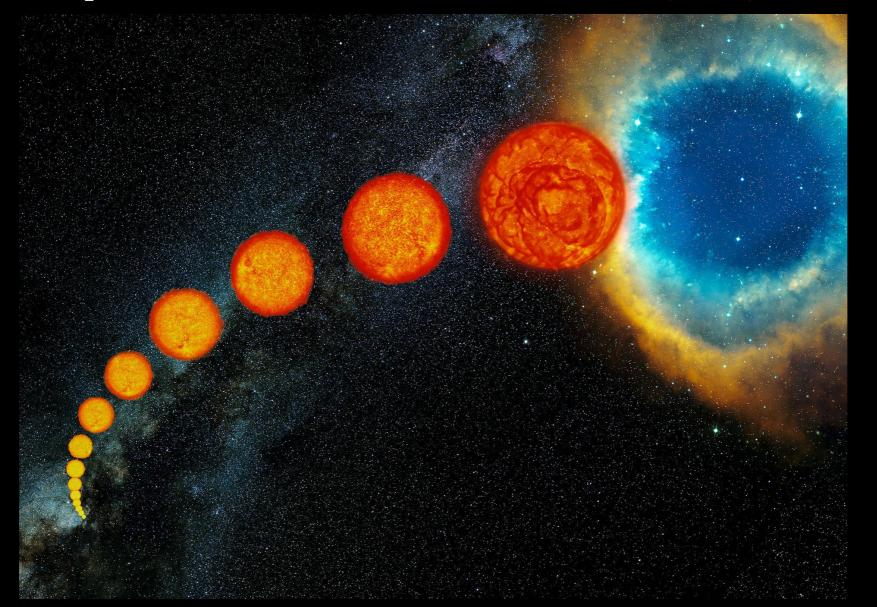


# The inorganic carbon cycle: a powerful mechanism that regulates climate.

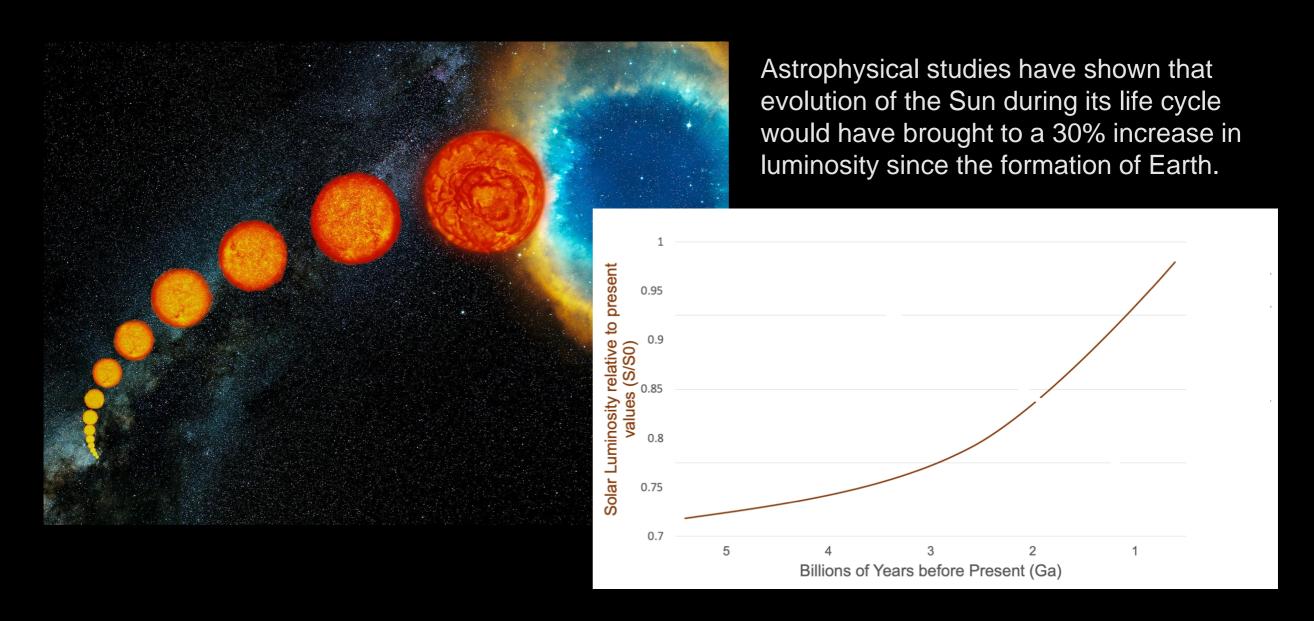
Without this mechanism, concentrations of CO<sub>2</sub> emitted by volcanoes would keep rising and, among many other consequences, this would cause extremely strong greenhouse effect.



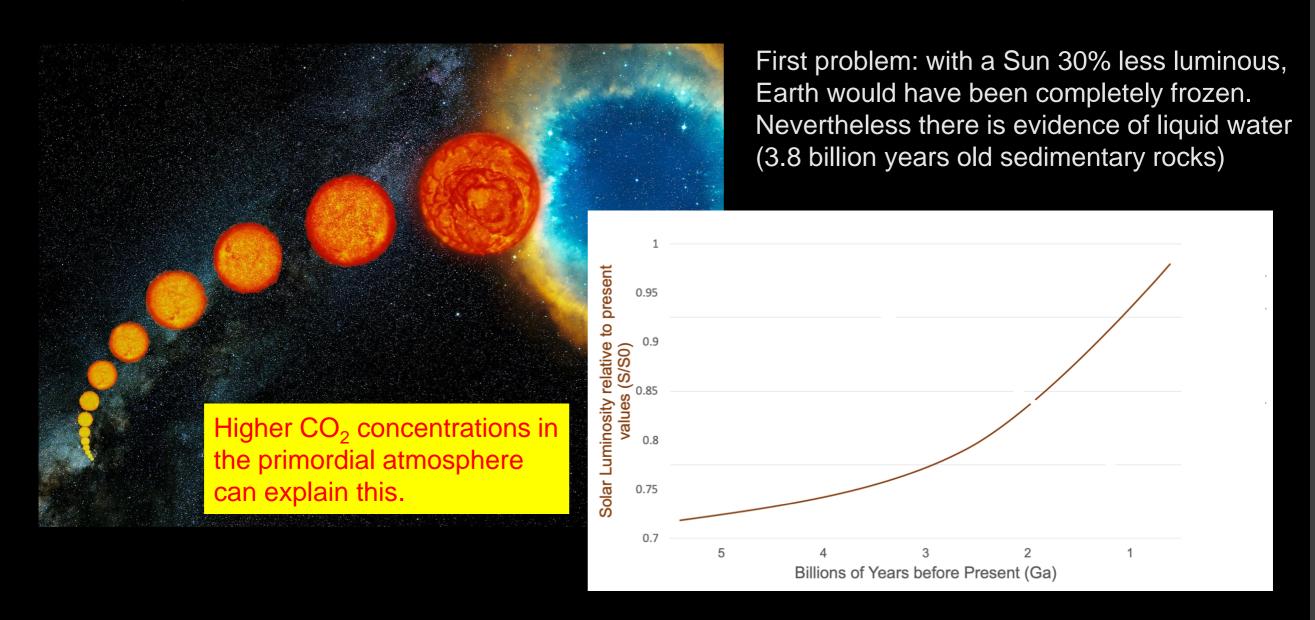
Sequestration of CO<sub>2</sub> by carbonate burial plays fundamental role in regulating Earth climate through time



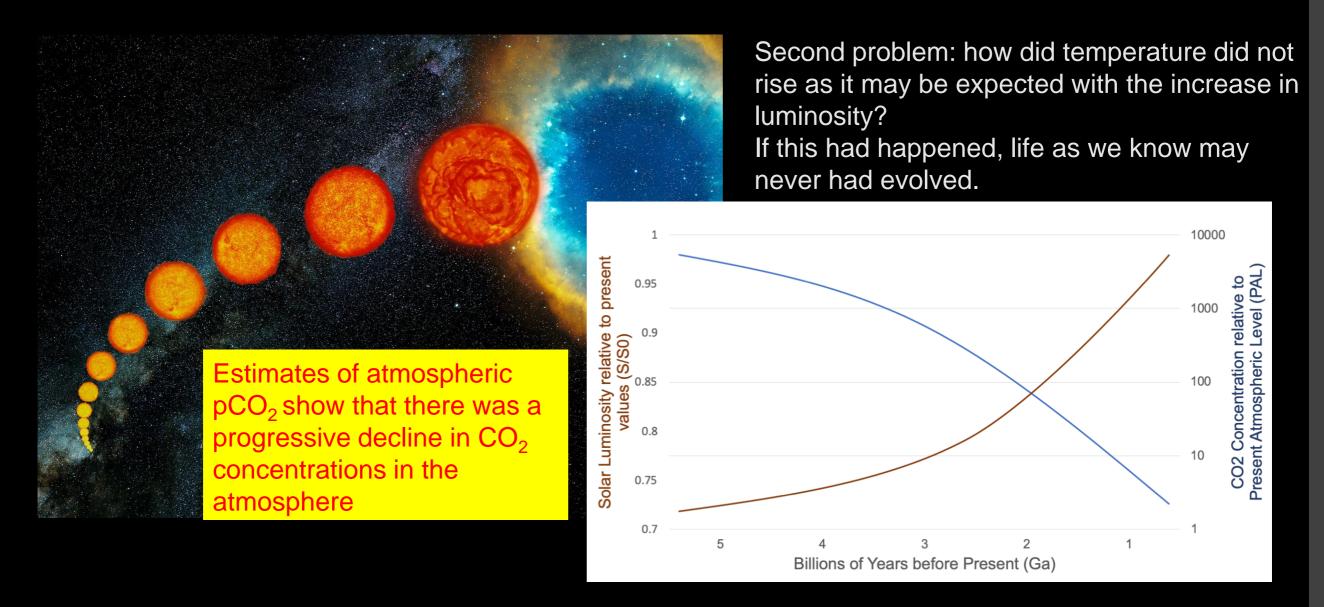
#### The faint young Sun paradox



#### The faint young Sun paradox

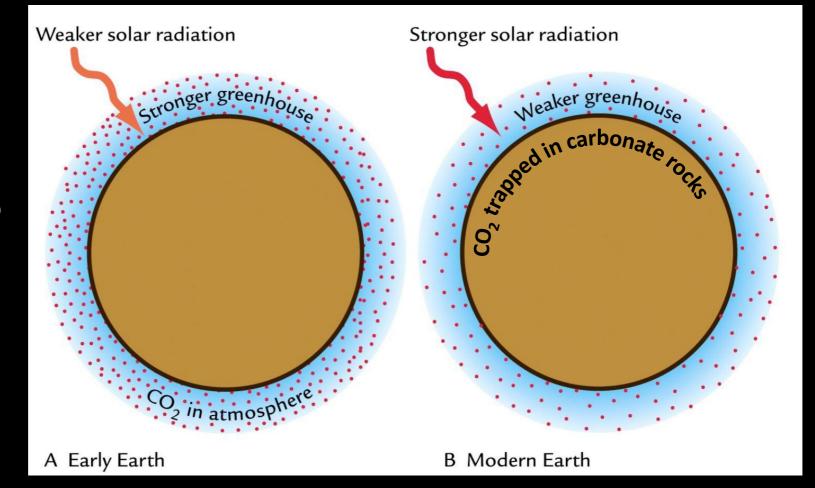


The faint young Sun paradox



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<sub>2</sub> 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



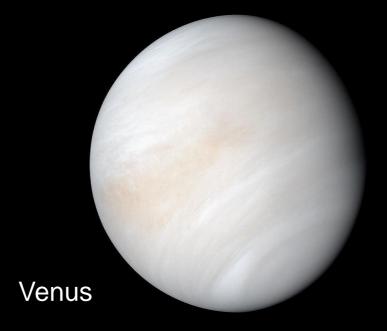
The carbon cycle is unique of planet Earth in the Solar System and exists because the distance from the Sun is such as liquid water is present and a C-cyle exists that is able to transfer back to the lithosphere part of the carbon that is emitted into the atmosphere by volcanoes. An example of planet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



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

Earth

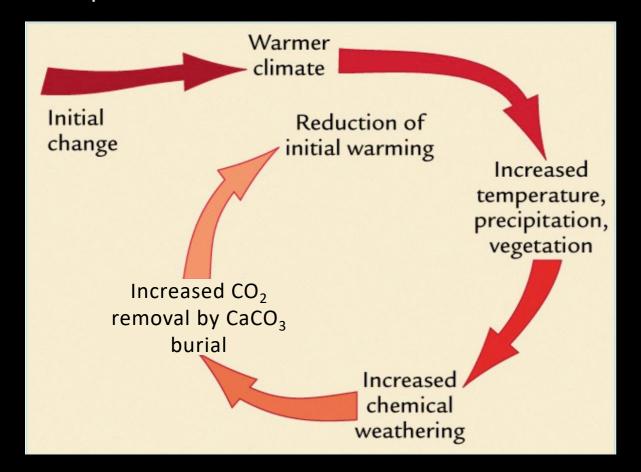
Life as we know it possible

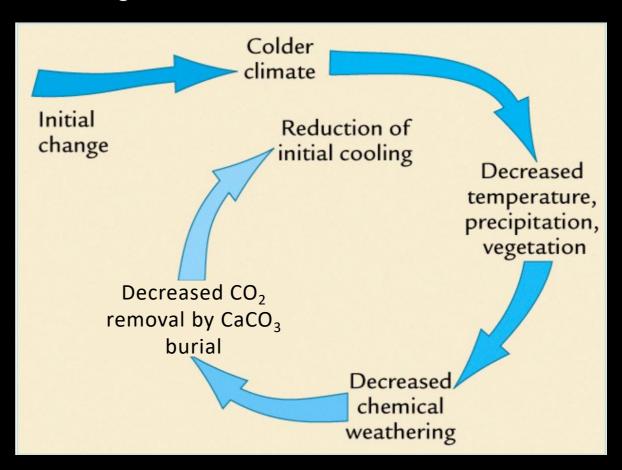


2 x10<sup>8</sup> Gt carbon in the atmosphere No C-cycle. All CO<sub>2</sub> emitted by volcanoes in the atmosphere

Life as we know it not possible

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

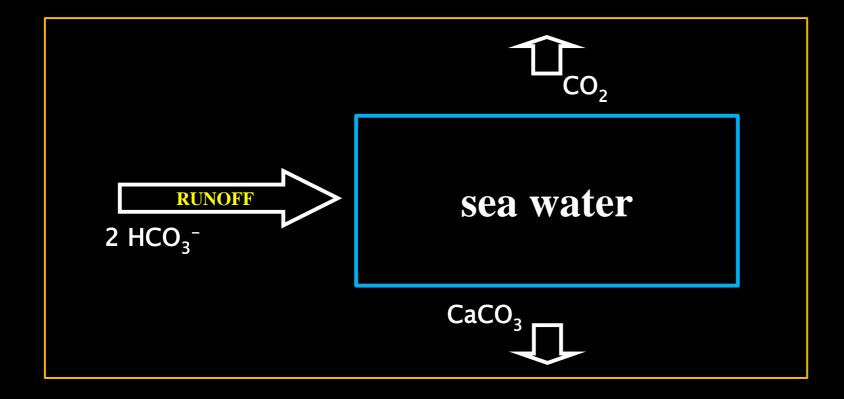




Thanks to the geological carbon cycle and the precipitation of carbonates in the oceans Earth's climate has a sort of thermostat that tends to buffer extreme oscillations in temperature! Let's look again at the precipitation reaction.

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

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



Precipitation releases CO<sub>2</sub>, while dissolution consumes CO<sub>2</sub>. 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 (10<sup>3</sup>)

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#### Carbon in the oceans

- normally we refer to inorganic carbon (TIC, total inorganic carbon)
- ...is present as CO<sub>2</sub> in gaseous solution;
- Reacts with seawater to give carbonic acid:

$$CO_2 + H_2O = H_2CO_3$$

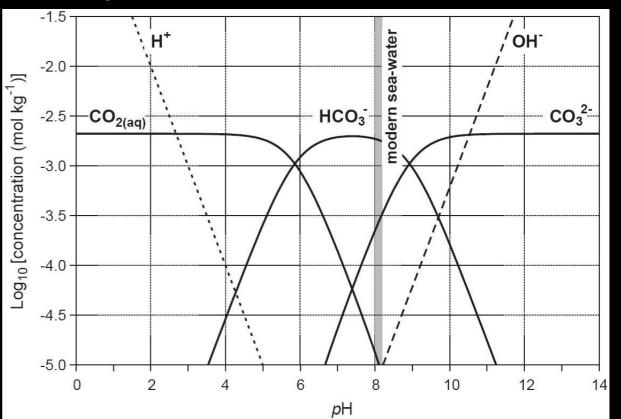
Carbonic acid dissociates:

$$H_2CO_3 \leftrightharpoons HCO_3^- + H^+ \leftrightharpoons CO_3^{2-} + 2H^+$$

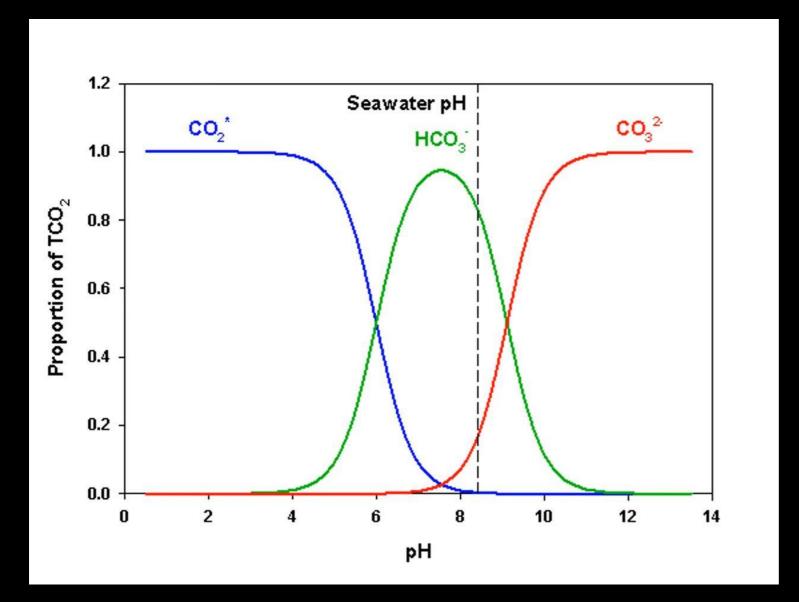
The form in which inorganic carbon is in the water depends on pH. In present oceans, it is mostly  $HCO_3^-$ .

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

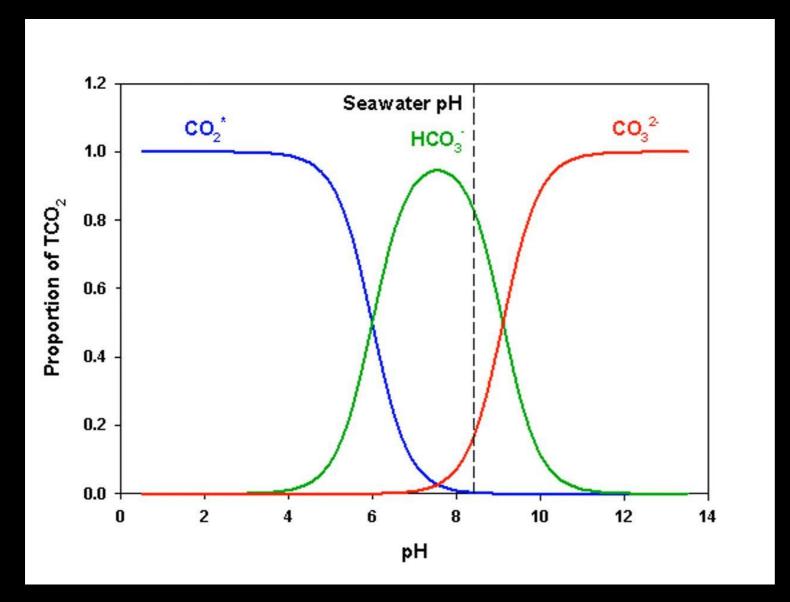
An important feature of the carbonate system in seawater is that it is a buffering system.

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.

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

#### Carbon in the oceans



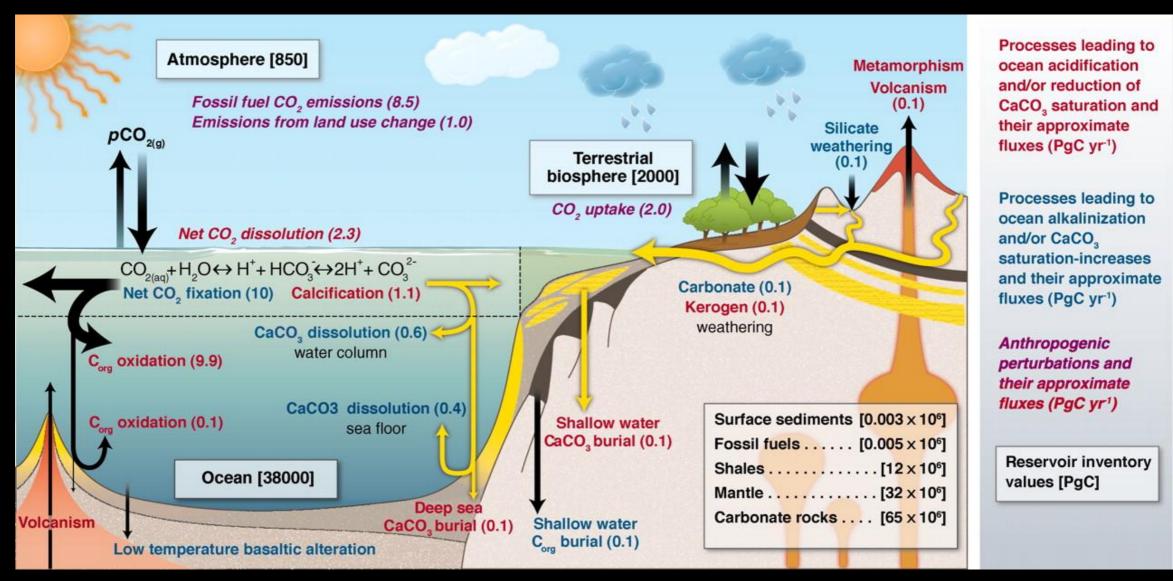
Partitioning of carbon species in seawater in function of pH

If pCO<sub>2</sub> in seawater increases, free hidrogen (H<sup>+</sup>) concentration increases, thus lowering pH (this is called acidification).

However, carbonate in seawater, if pH decreases, tends to dissolve, forming free calcium (Ca<sup>2+</sup>) ions and free bicarbonate  $(HCO_3^-)$  ions.

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

This creates the buffering effect of carbonate system in seawater.



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

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300 million year old ripples next to 300 minute old ripples. Photo credits <u>lan Kane</u>



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.

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.

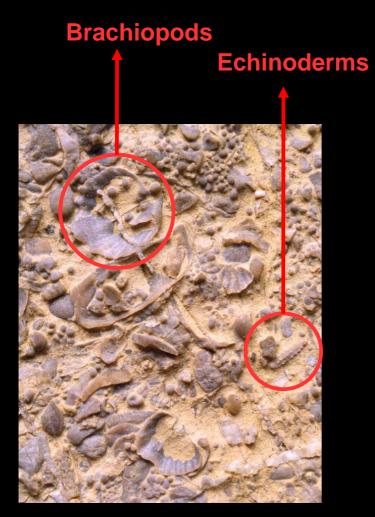
#### Three main consequences:

- 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)

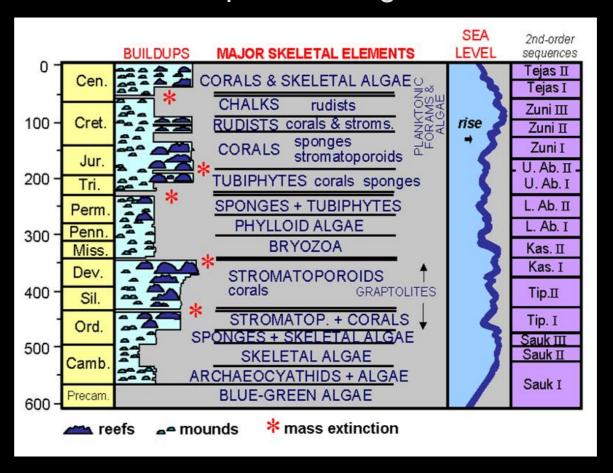


# Carbonates: the biological factor



Carbonate rocks may contain skeletal grains

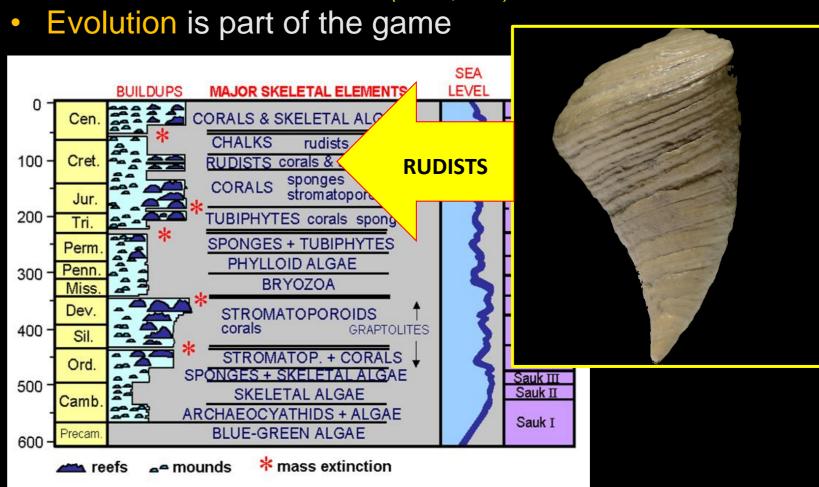
- "Carbonates are born, not made" (James, 1979)
- Evolution is part of the game



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

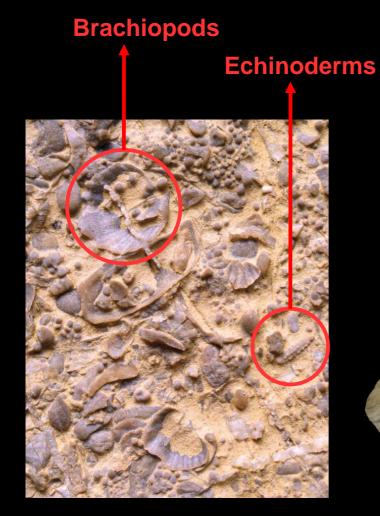
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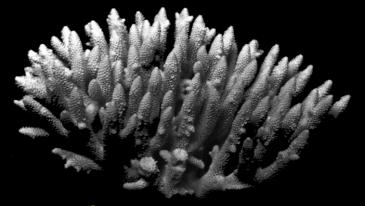
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# Carbonates: the biological factor



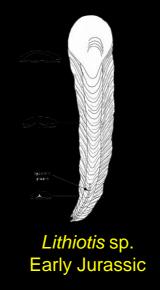
Carbonate rocks may contain skeletal grains

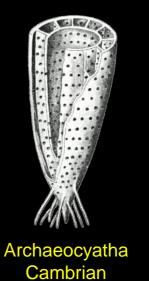
Reef-building organisms with carbonate shells or skeletons were there since the Precambrian. ecological preferences may have changed.



Scleractinian coral Cenozoic to present



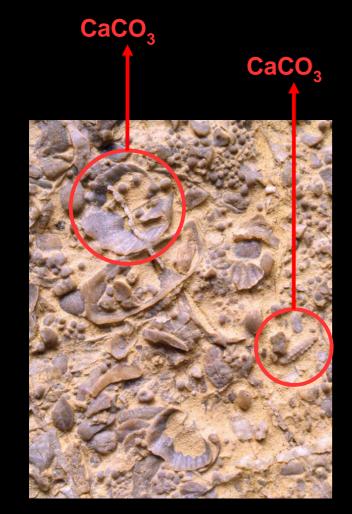






Stromatolite Precambrian

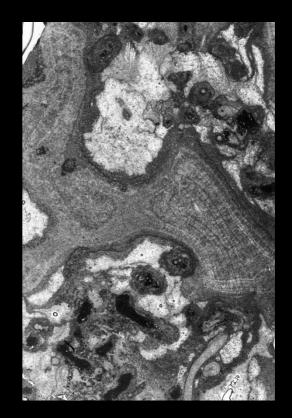
#### Carbonates: the chemical factor



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).

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



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!

