Carbonate Minerals and Dynamic Carbon Cycling

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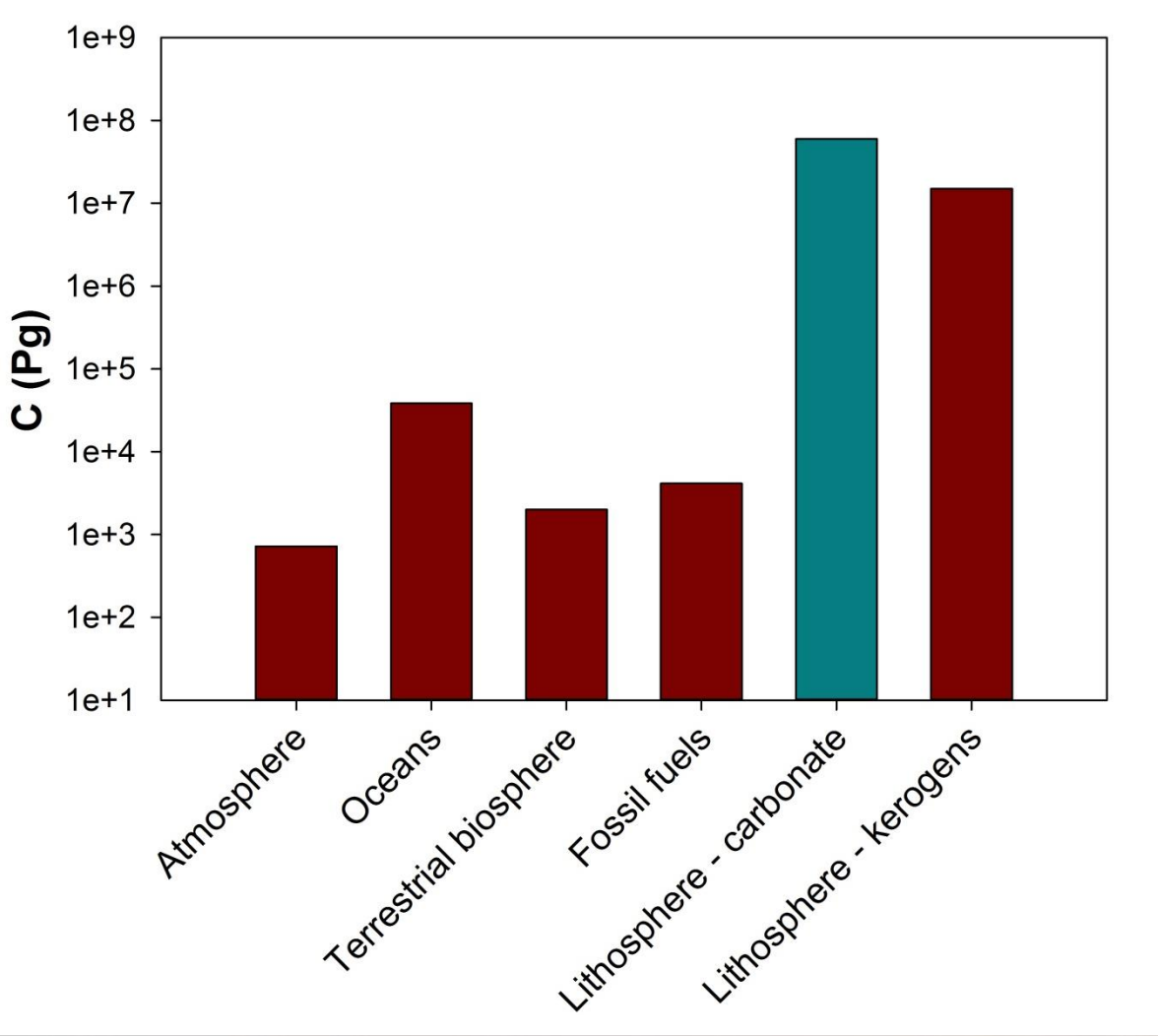
Funding

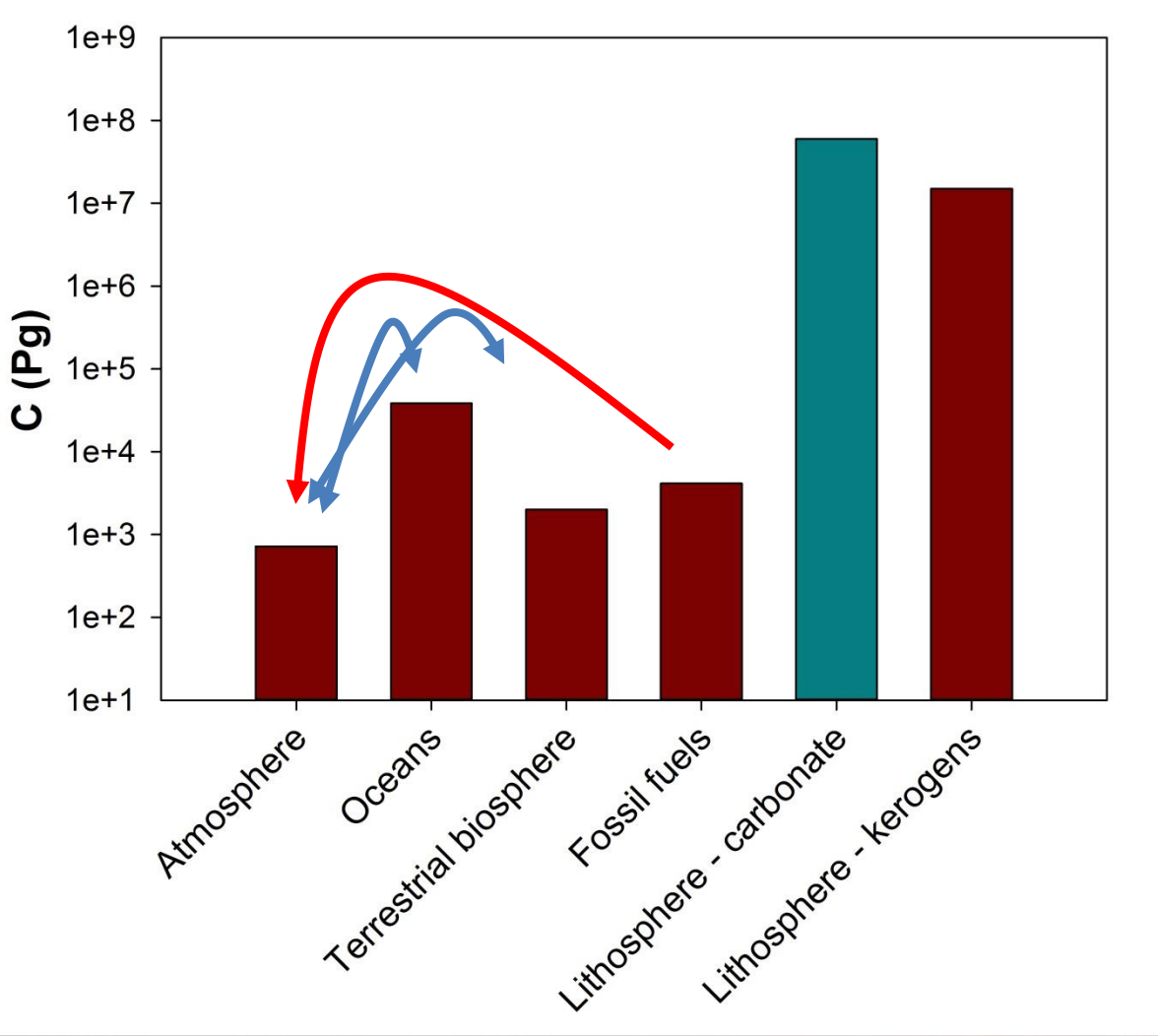
Global Carbon Reservoirs



- Carbonate rocks comprise earth's largest C reservoir
  - ~10^8 Pg
  - ~$5x10^4$ ocean
  - ~10^3 atmosphere

Data from Falkowski et al., 2000, Science

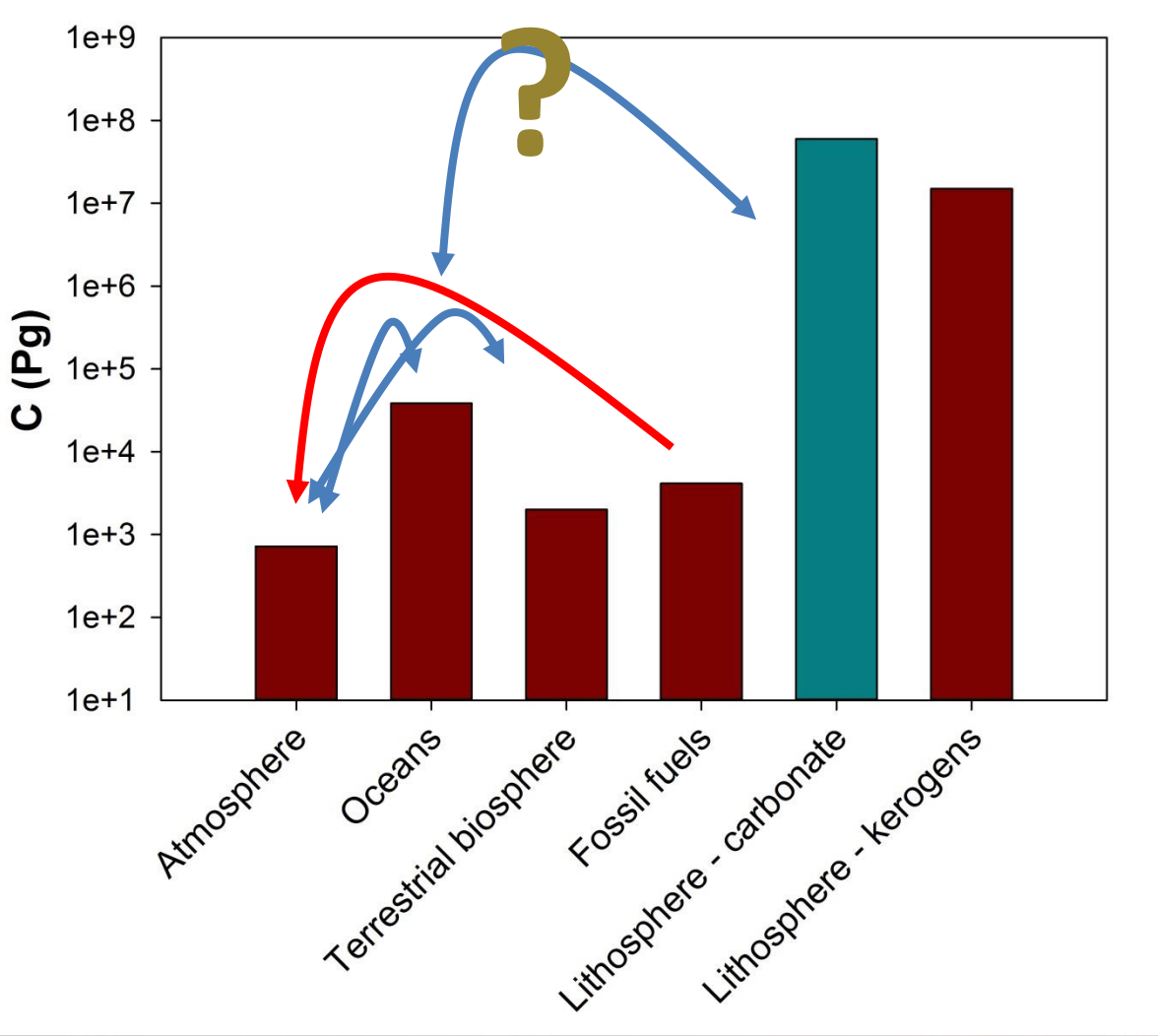
Global Carbon Cycle



- Carbonate rocks comprise earth's largest C reservoir
  - ~10^8 Pg
  - ~$5x10^4$ ocean
  - ~10^3 atmosphere
- Small reservoirs most dynamic
- Anthropogenic CO_2 impacts cycle

Data from Falkowski et al., 2000, Science

Today's Session Topic

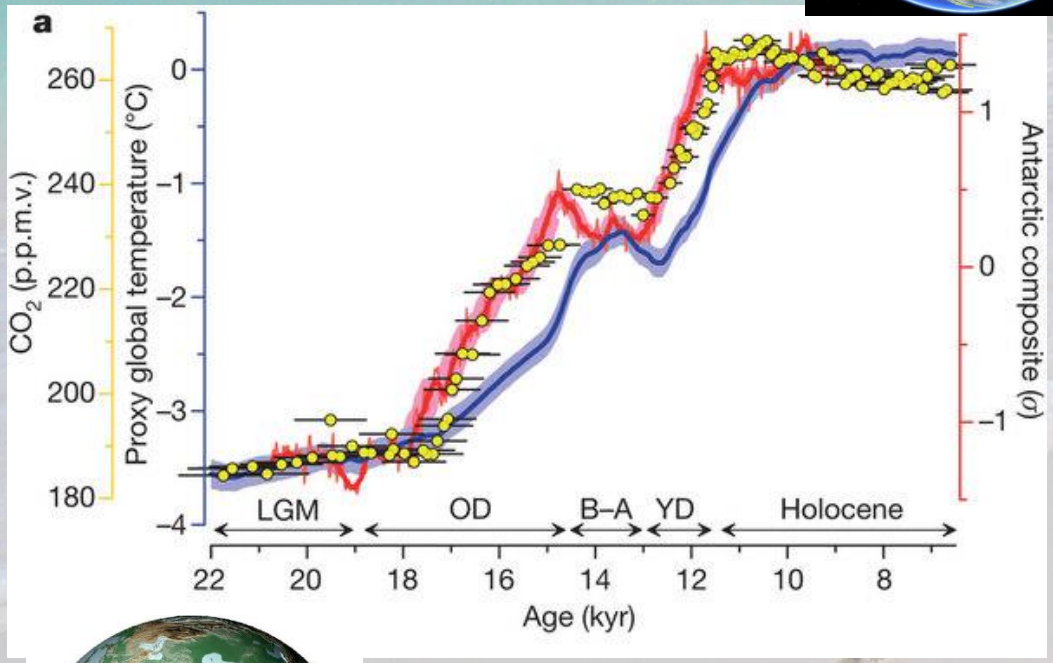


- Does the carbonate mineral reservoir interact with the global carbon cycle?

Data from Falkowski et al., 2000, Science

Impacts

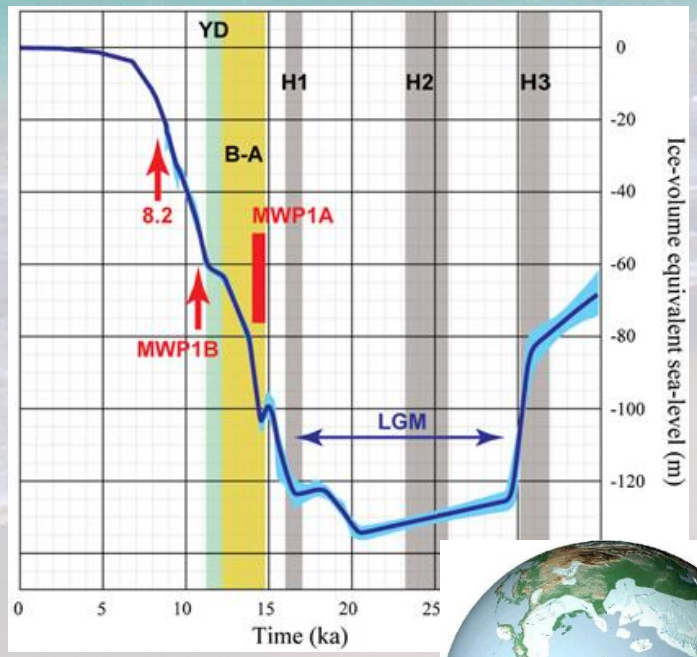
Temperature & CO_2



Forward in time →

Shakun et al., 2012, Nature

Sea Level



← Forward in time

Lambeck et al., 2014, PNAS

Dynamics

- **Carbonate dissolution by carbonic acid:**

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

  - Dissolution reaction: Atmospheric CO_2 sink
  - Precipitation reaction: Atmospheric CO_2 source

Dynamics

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  - Precipitation reaction: Atmospheric CO_2 source

- **Silicate weathering and coupled calcite precipitation**

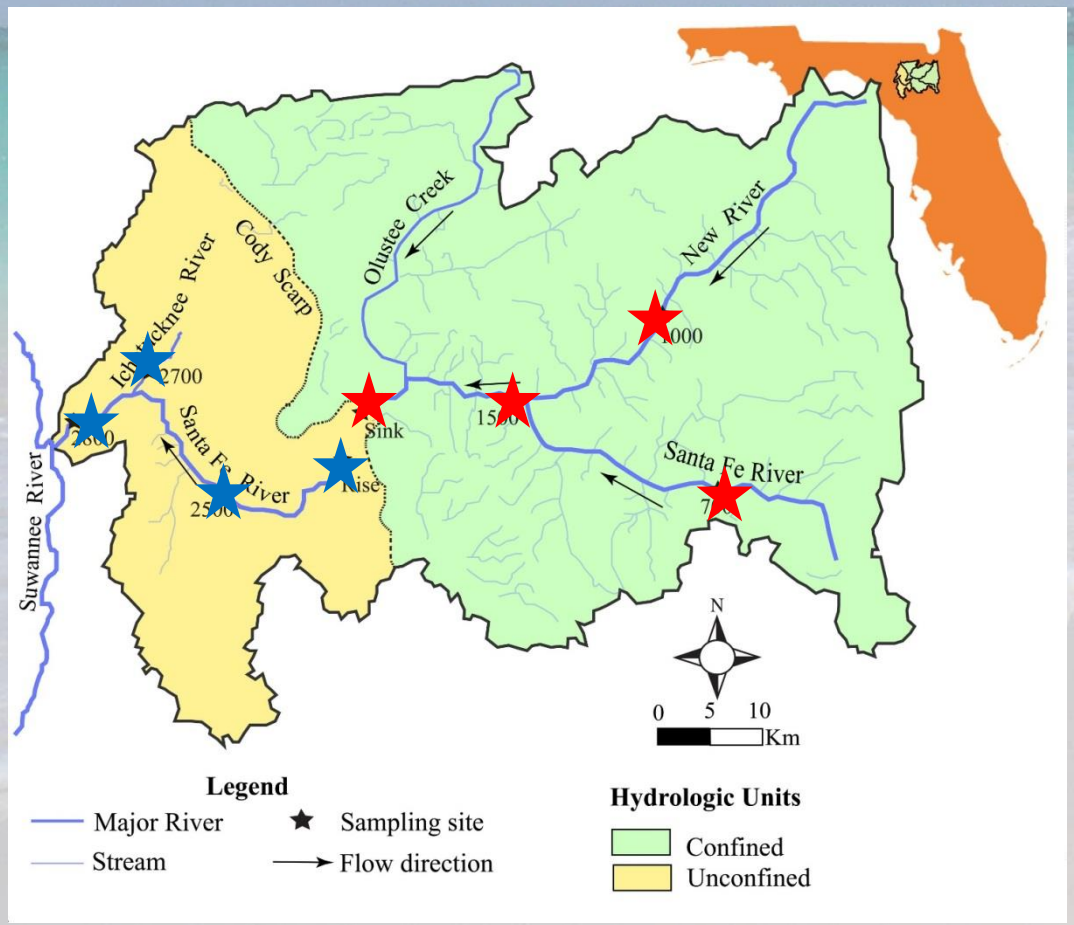
$$CaSiO_3 + 2CO_2 + H_2O \rightarrow Ca^{+2} + 2HCO_3^- + SiO_2$$
$$Ca^{+2} + 2HCO_3^- \rightarrow CaCO_3 + H_2O + CO_2$$

$$CaSiO_3 + CO_2 \rightarrow CaCO_3 + SiO_2 \text{ (phytoplankton – rapid sink)}$$

$$CaSiO_3 + CO_2 \leftarrow CaCO_3 + SiO_2 \text{ (metamorphism – slow source)}$$

Berner et al., 1983, Am J Sci

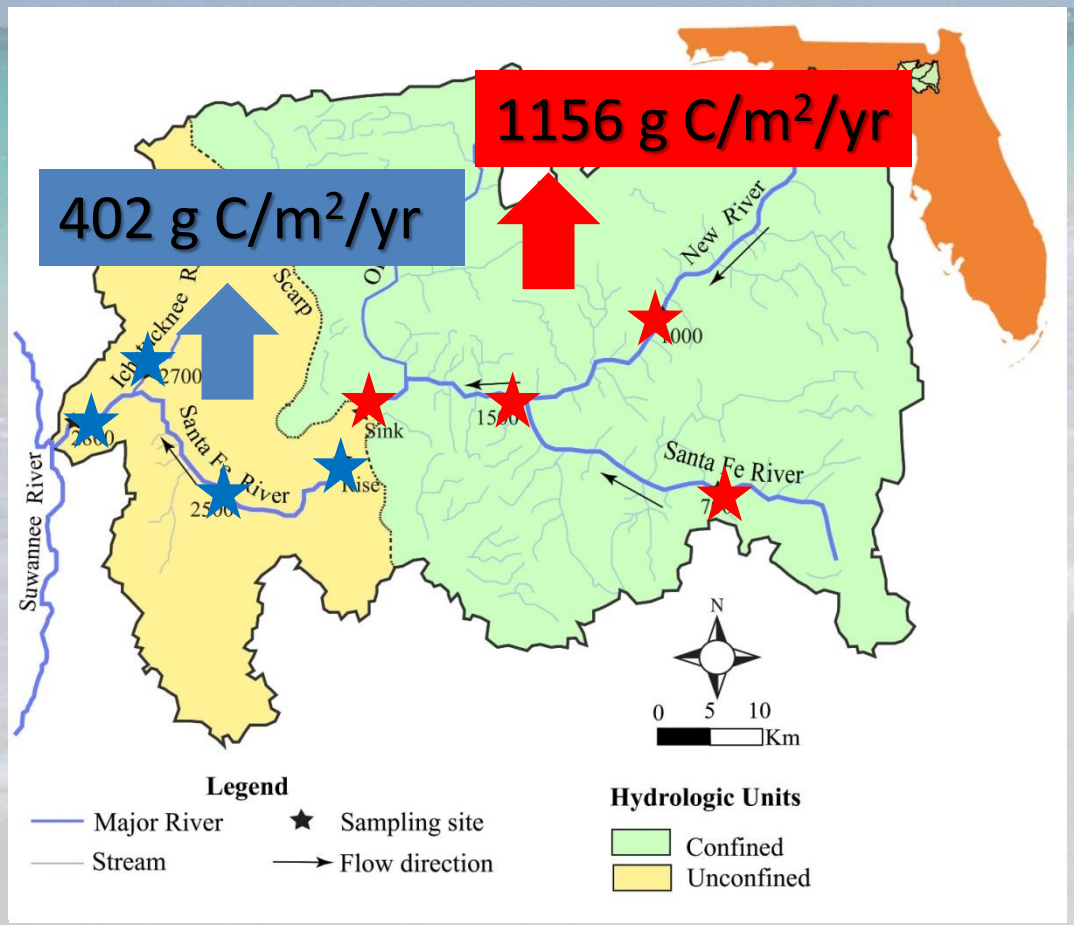
Carbonate-Silicate Weathering



- CO_2 fluxes
  - Measured at 3 distinct flow rates
  - Measured at multiple gaging stations

Khadka et al., 2014, J. Hydro.

Carbonate-Silicate Weathering



- CO_2 fluxes
  - Measured at 3 distinct flow rates

- Siliciclastic watershed 3 X higher CO_2 fluxes than carbonate
- Buffering of respired CO_2

Khadka et al., 2014, J. Hydro.

Dynamics

- **Carbonic acid dissolution:**

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

  - Dissolution reaction: Atmospheric CO_2 sink
  - Precipitation reaction: Atmospheric CO_2 source

- **Sulfuric acid dissolution:**

$$H_2S + 2O_2 + CaCO_3 \rightarrow SO_4^{2-} + Ca^{2+} + H_2O + CO_2$$

  - Net CO_2 source to atmosphere

Two Example of S-related Dissolution

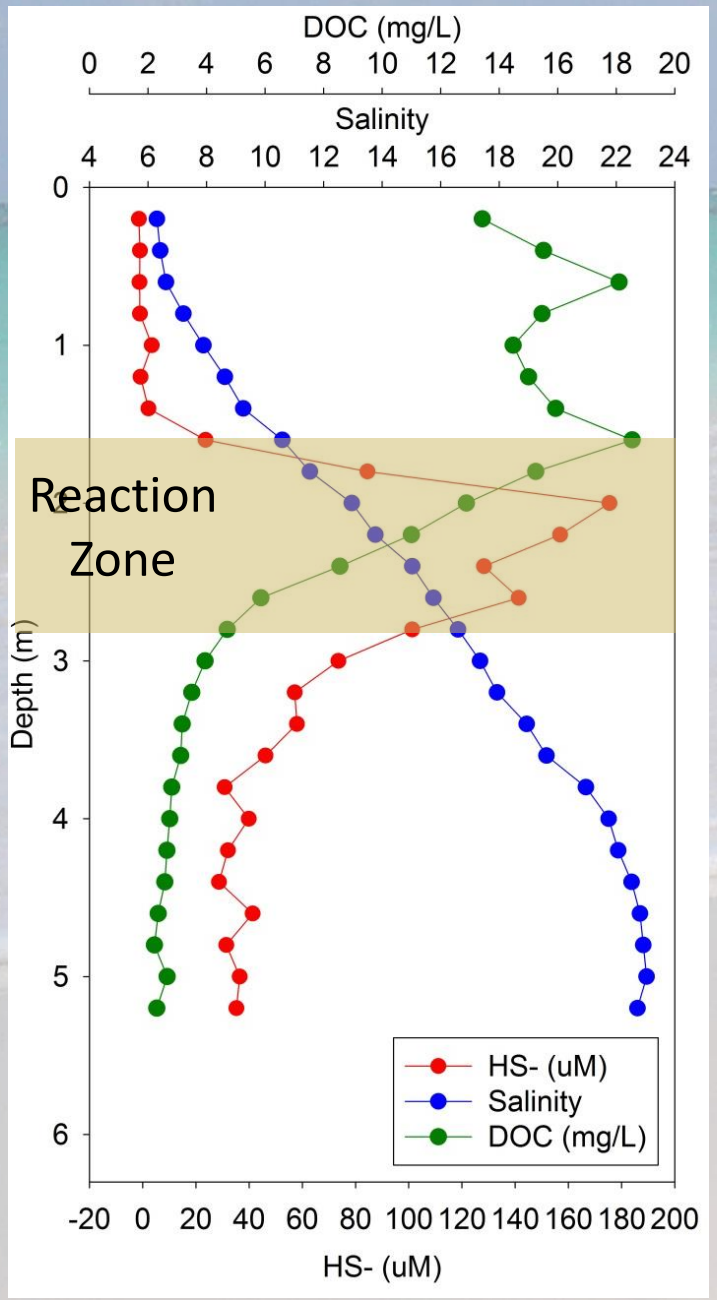
- Carbonate & Silicate
- All related to redox reactions
  - SO_4^{2-} reduction and FeS_2 oxidation

Lake George
Blue Hole
Rum Cay,
Bahamas

Angelita Cenote
Quintana Roo, Mexico

Greenland
Watersheds

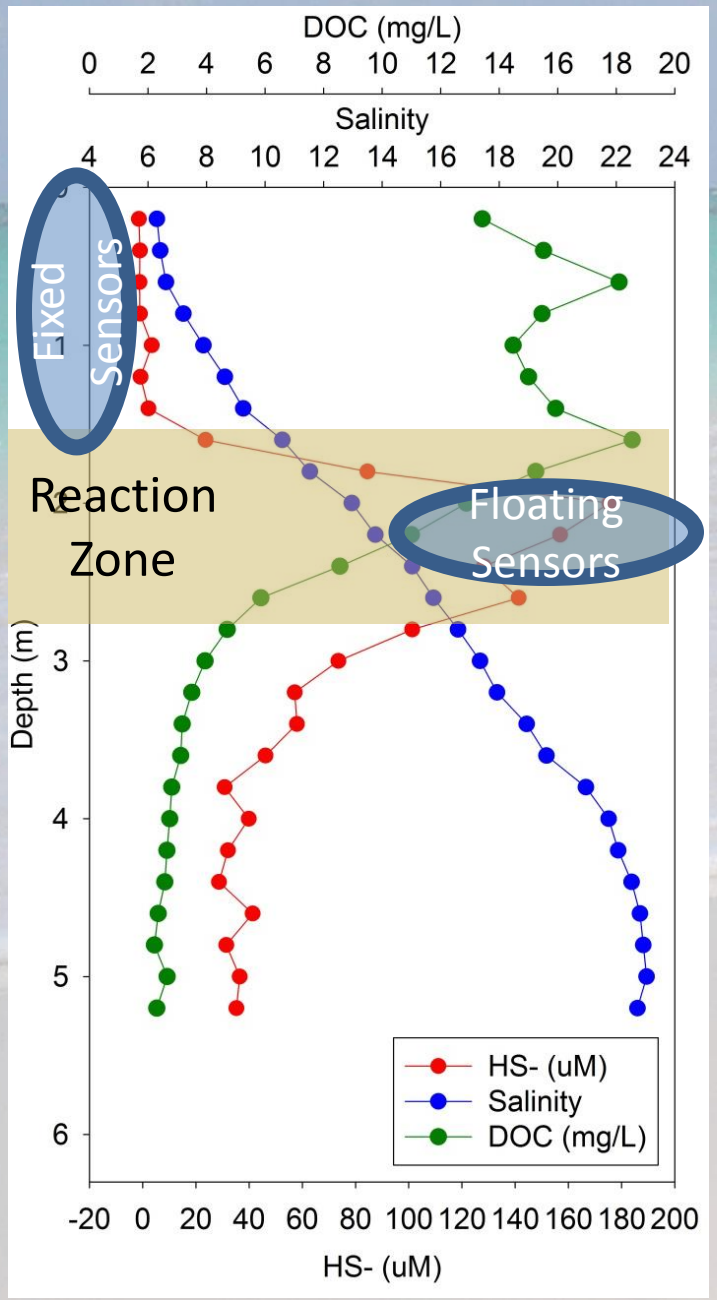
Ink Well Blue Hole, Bahamas



- San Salvador Island
  - Small (~50 km^2) island
  - Isolated carbonate platform
- At pycnocline/halocline:
  - Organic carbon trapped
  - Sulfate reduction increases sulfide concentrations
  - Sulfide diffuses upward and is oxidized
  - Decreases pH

Pain et al., in prep.

Ink Well Blue Hole, Bahamas

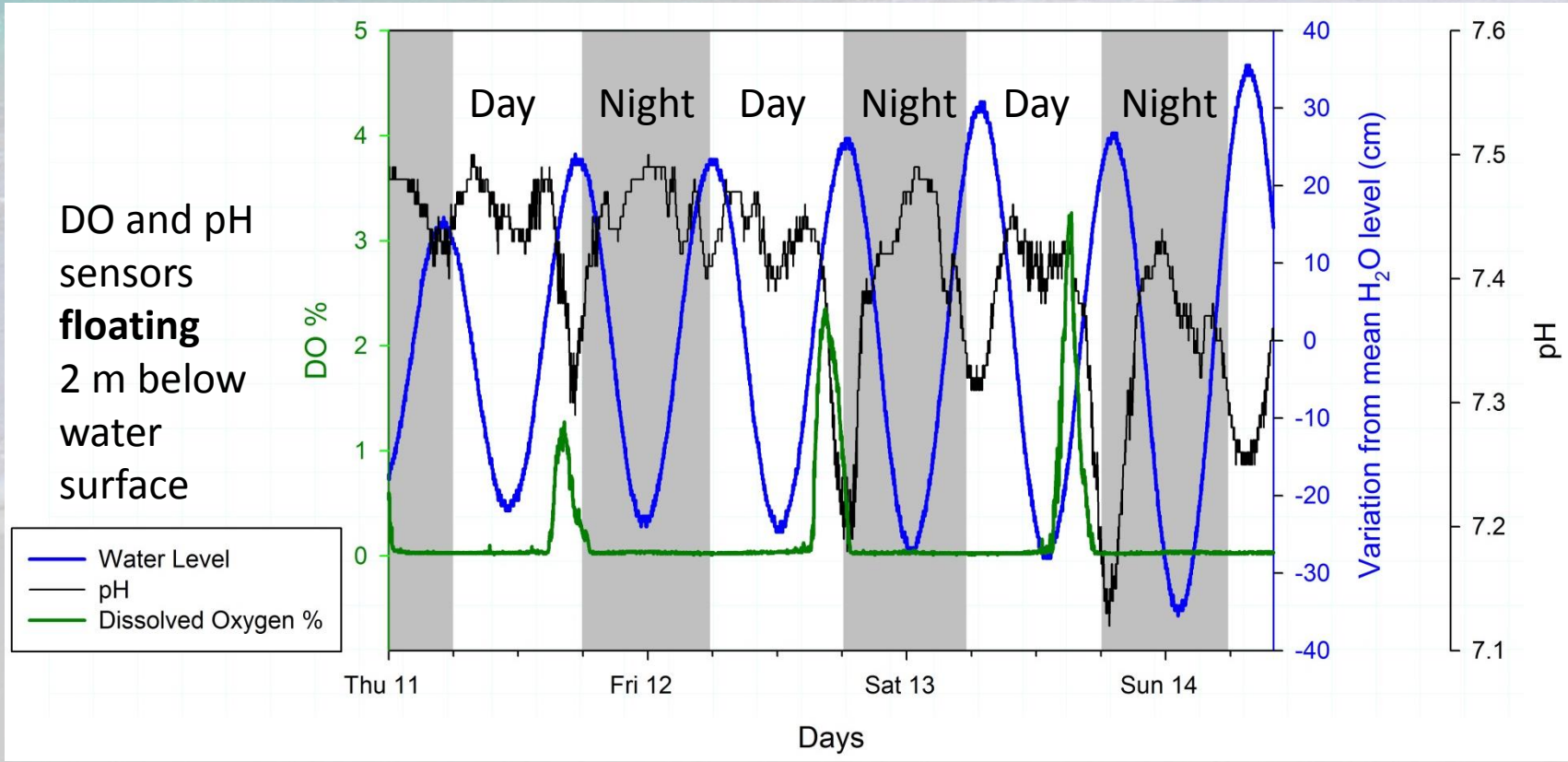


- Is system static or dynamic?
- San Salvador Island
  - Small (~50 km^2) island
  - Isolated platform
- At pycnocline/halocline:
  - Organic carbon trapped
  - Sulfate reduction increases sulfide concentrations
  - Sulfide oxidized as diffuses upward to oxic
  - Decreases pH

Ezell et al., in prep.

Dynamics at pycnocline

- Low tide increase radiation and photosynthetic DO production
- pH drops follows DO production – DO consumption and sulfide oxidation

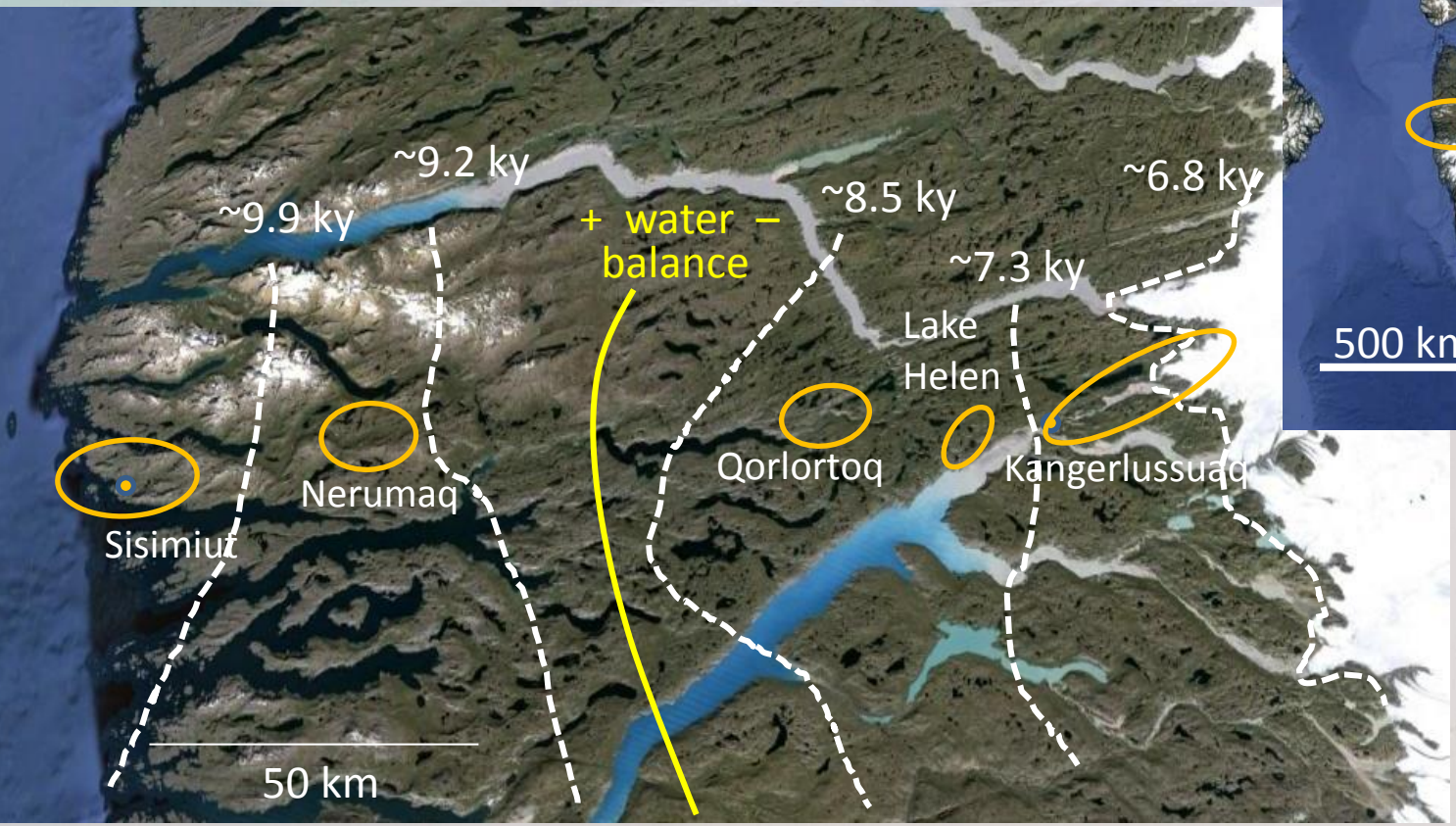


Ezell et al., in prep.

Greenland watershed

~125 km transect coast to GrIS

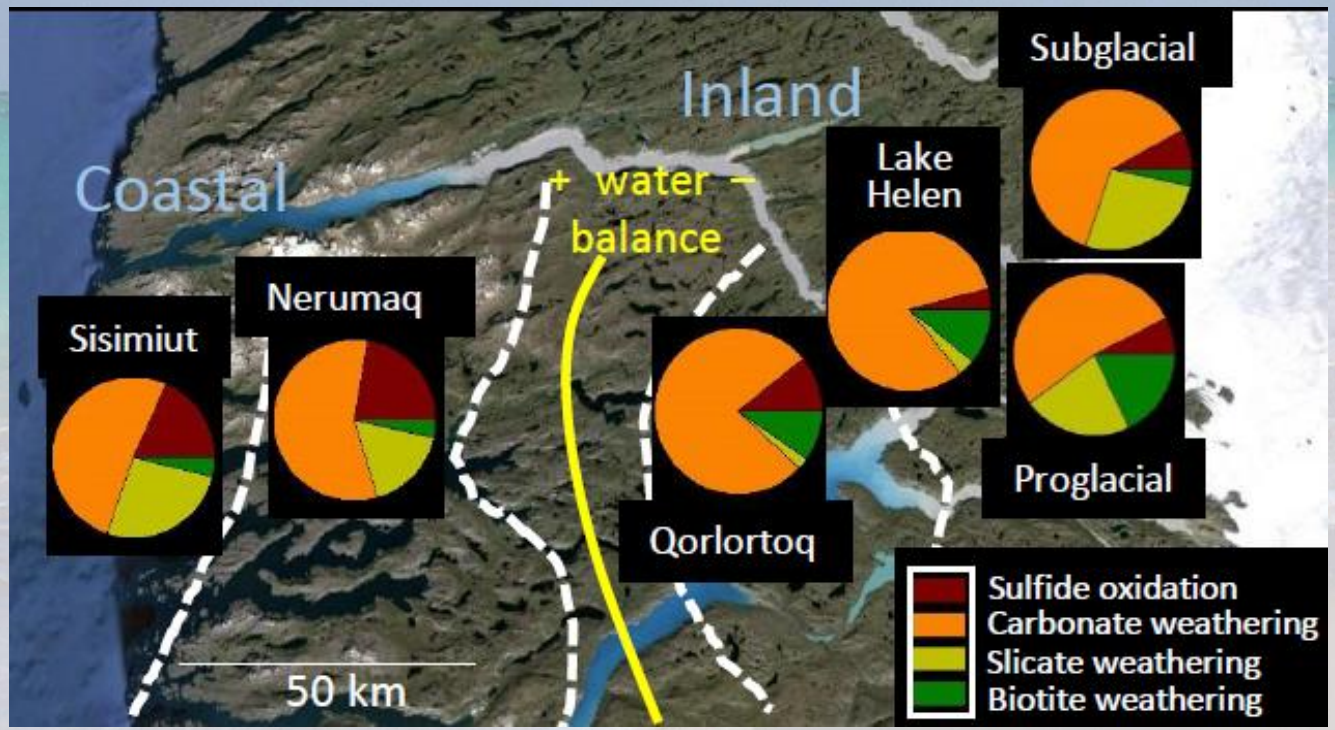
- Similar lithologies
- Gradient in exposure age of moraines
- Gradient in precipitation vs. evaporation



Google Earth

Scribner et al., 2015, GCA

Weathered Minerals



- Carbonate mineral primary mineral weathered
  - Trace content of bedrock
- Weathering enhanced by sulfide mineral oxidation

Deuerling et al., in prep.

Conclusions

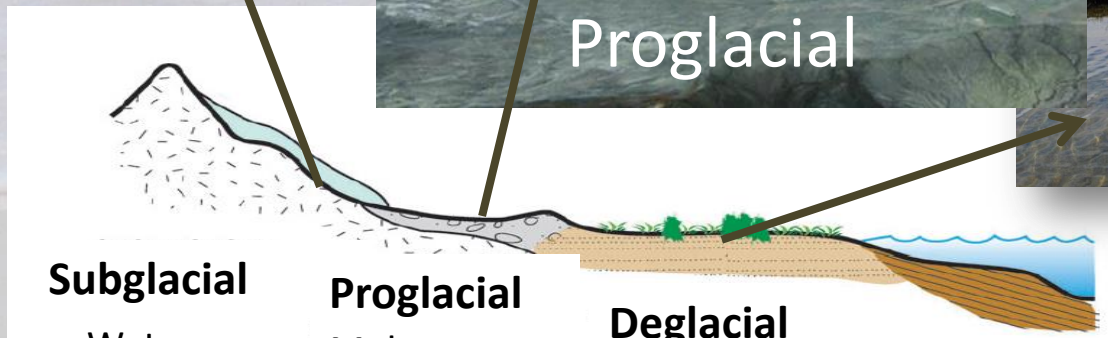
- Carbonate dissolution/precipitation:
  - Multiple mechanisms for interactions with C cycle
- Impacts depend on:
  - Time scales – rapid so short term changes
  - Spatial scales – small regions, but globally varied
- Talked only about mechanism
  - What are magnitudes of fluxes???

Stay with us…

Greenland Watersheds

Increasing exposure age/extent of weathering

Watershed types:



Subglacial

Water system under the ice

Proglacial

Melt water discharged from the ice sheet

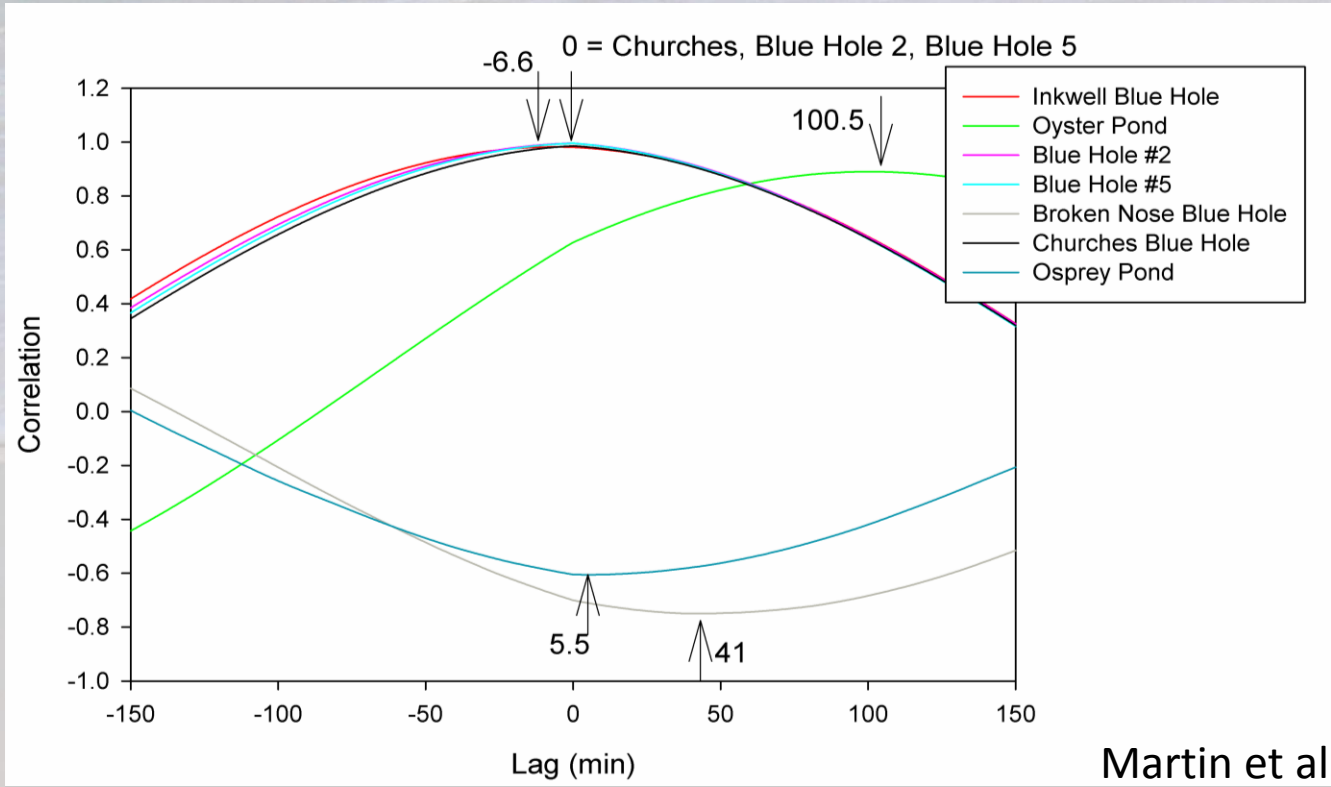
Deglacial

Water from annual precipitation and permafrost melt

Modified from Anderson, 2007, Ann. Rev. Earth Planet Sci

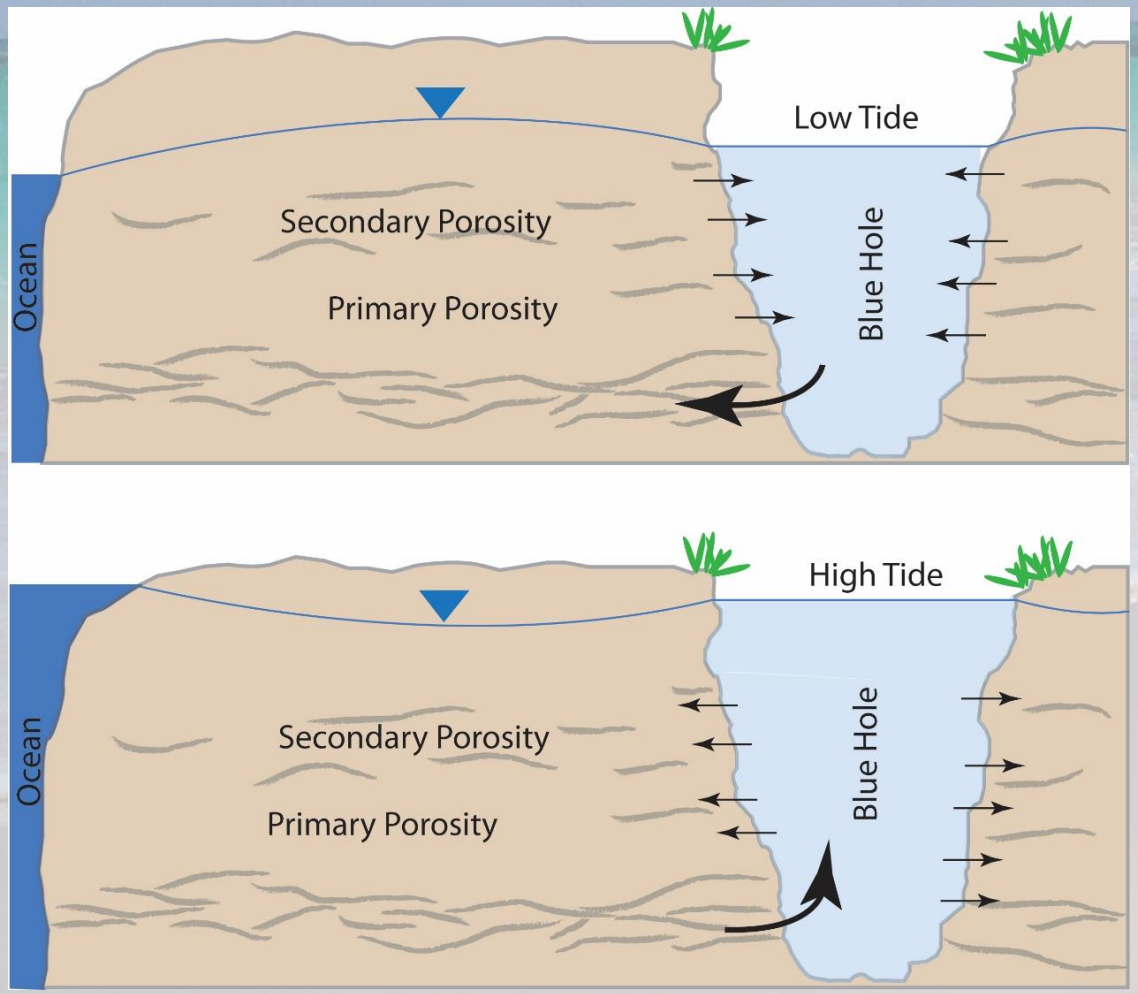
Lags between inland water and ocean

- Cross correlations of ocean and surface water elevations:
  - 2 week long time series
- Variable tidal lags reflect heterogeneous permeability (K)
- Variable K = Undulating water table = head gradients



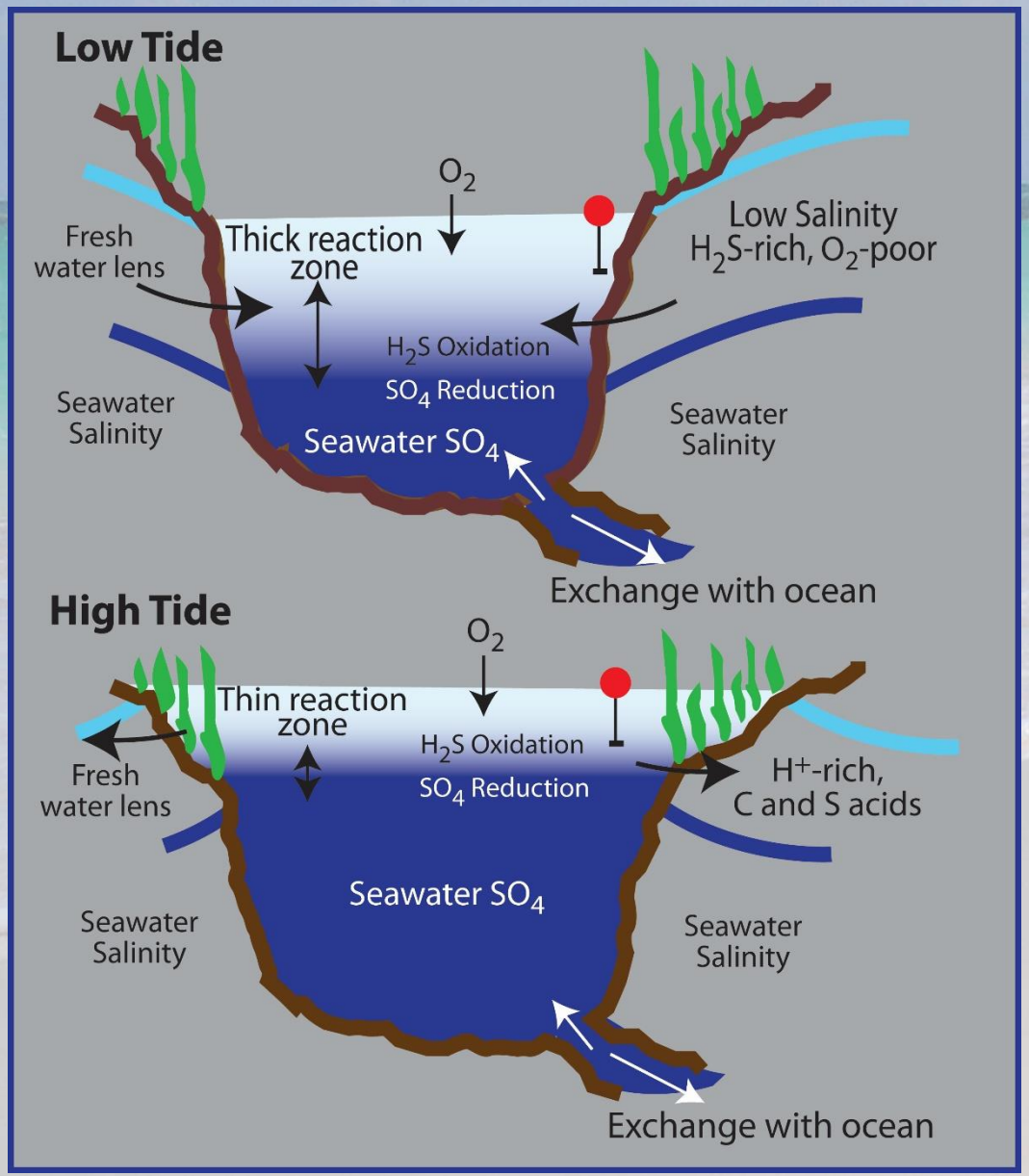
Martin et al., 2012 J Hydro

Tidal pumping



- At low tide:
  - water table > ocean and blue holes elevations
  - Water drains from aquifer to blue hole
- At high tide:
  - Water table < ocean and blue holes elevations
  - Water drains from blue hole to aquifer

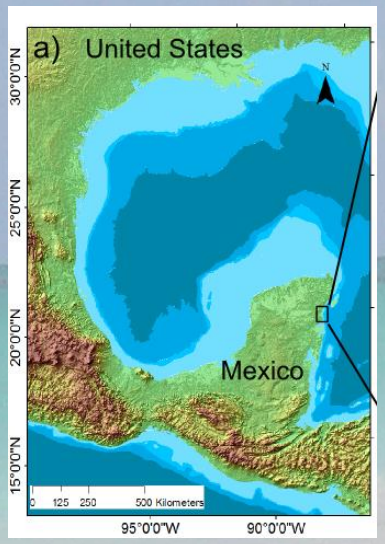
Martin et al., 2012 J Hydro

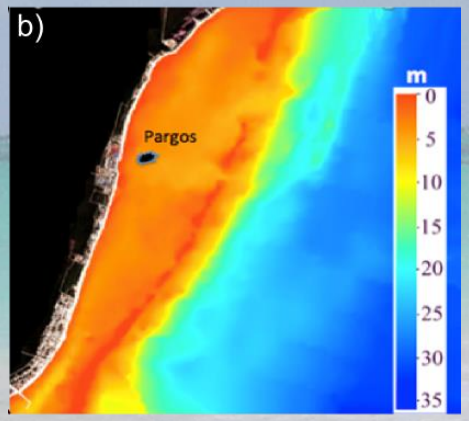


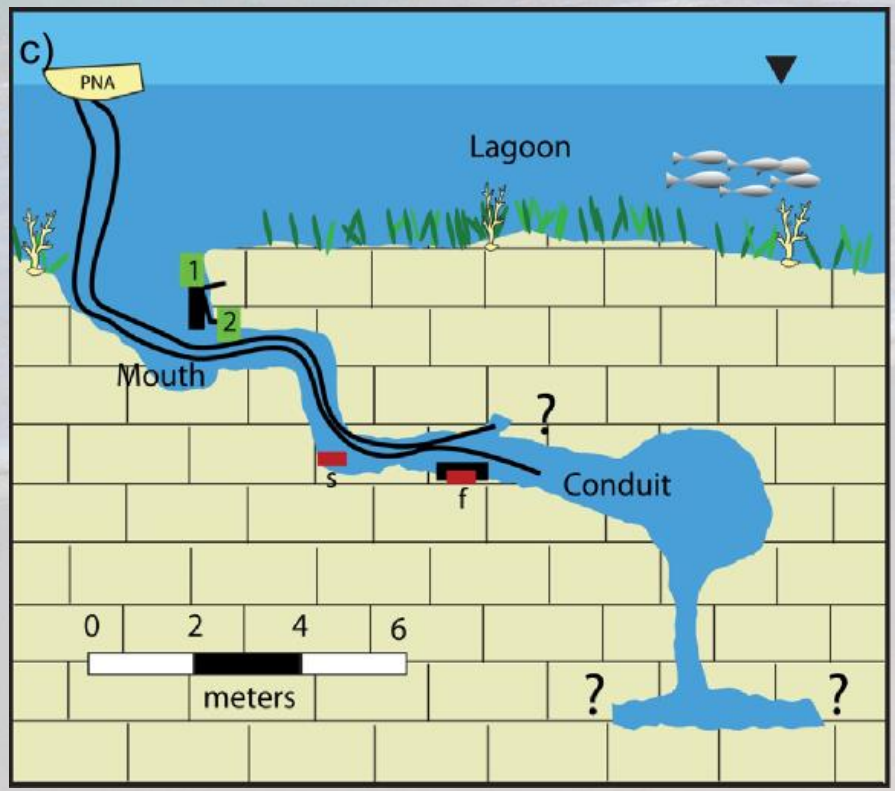
Summary

- Dissolution results from interplay of photosynthesis, hydrology, and redox/acid reactions
- What are connections with and impacts to coastal ocean?
- How are coastal solute fluxes, importantly nutrients, affected by these processes?

Discharge End – offshore springs





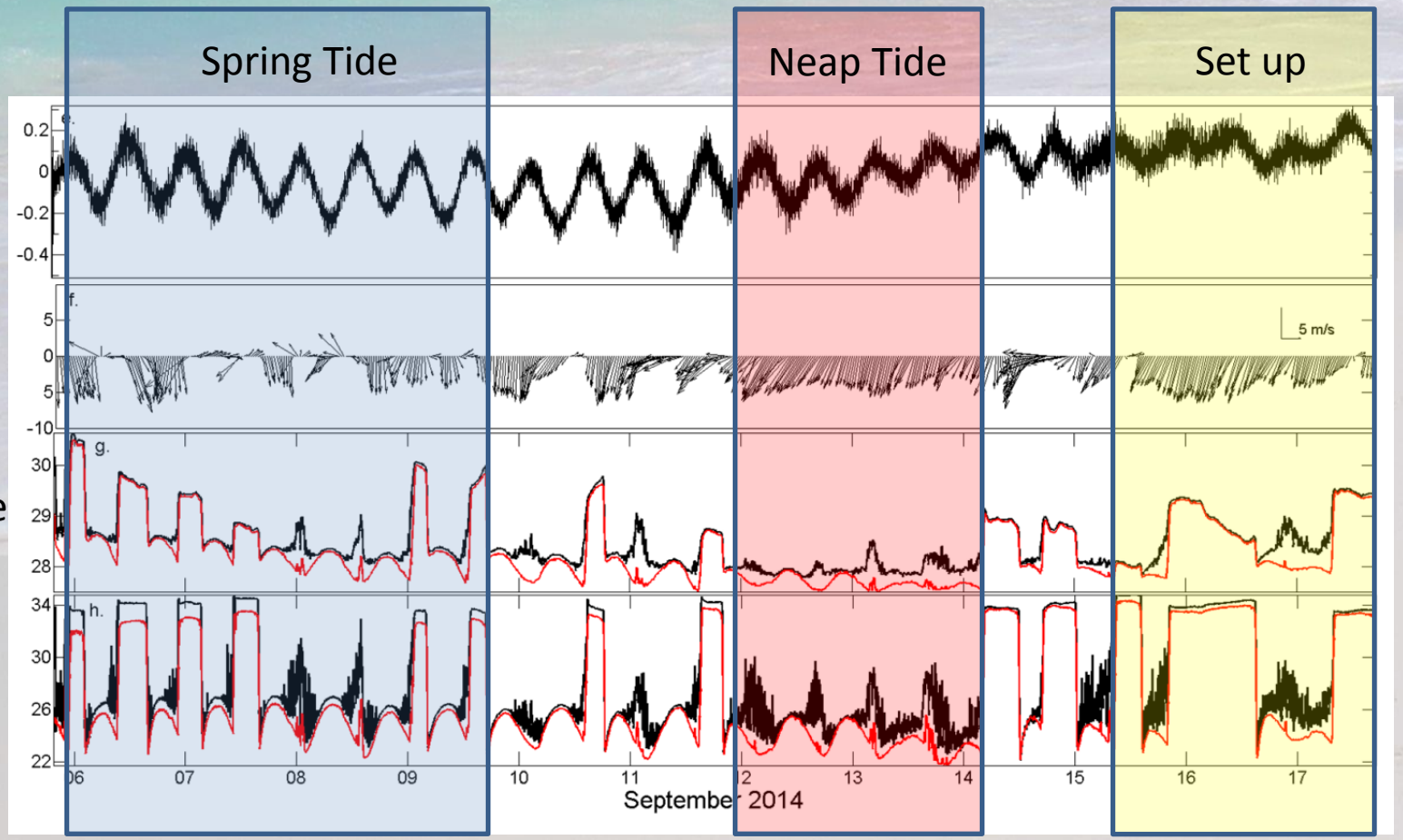


- Cave system offshore Yucatan Peninsula
- No surface drainage to oceans
- Multiple springs including Pargos Spring:
  - Cave exploration and instrumentation within cave and lagoon
  - Grab samples from within cave and lagoon

e.g., see Null et al., 2014 Cont Shelf Res

Two week time series

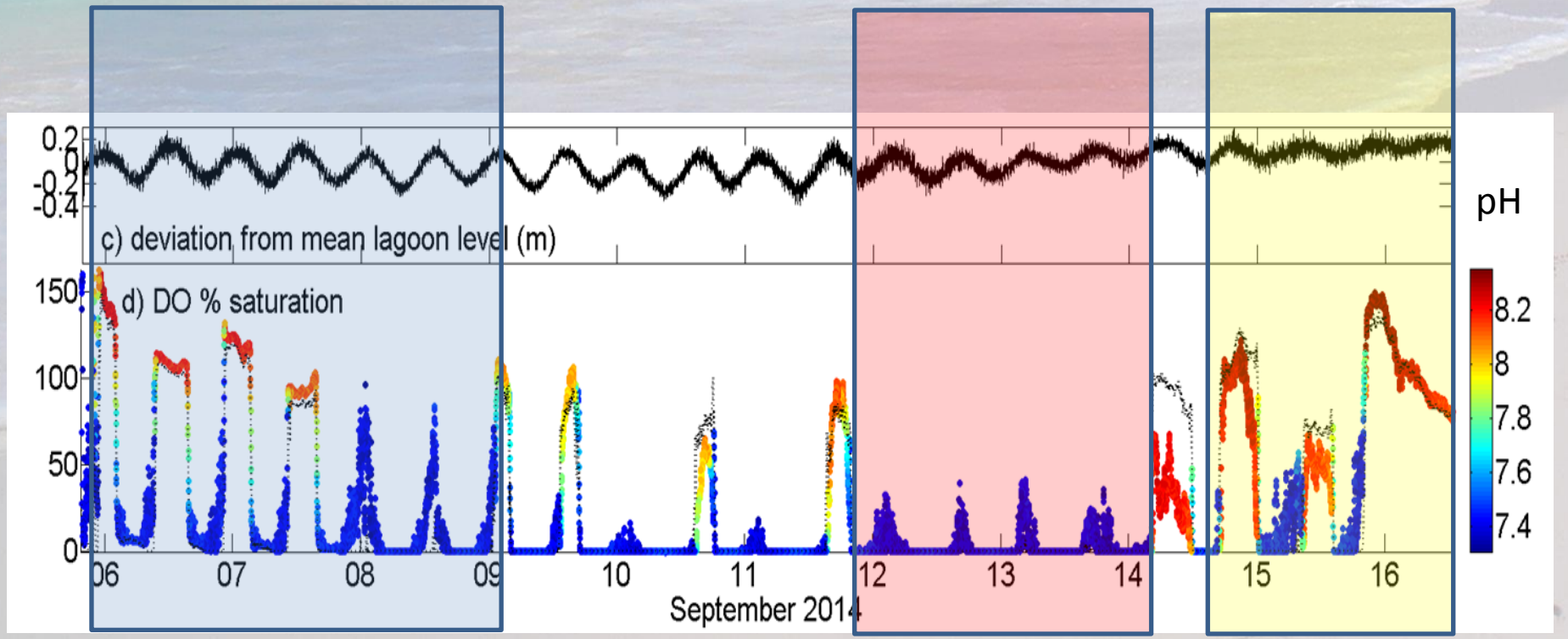
- T and S show reversing flow at spring
- Reversal frequency controlled by tides (spring/neap) and winds
  - Discharge when SL < 8 cm above average
  - Recharge when SL > 8 cm above average (20 – 30 yr SLR)



Young et al., in review

Reactive components

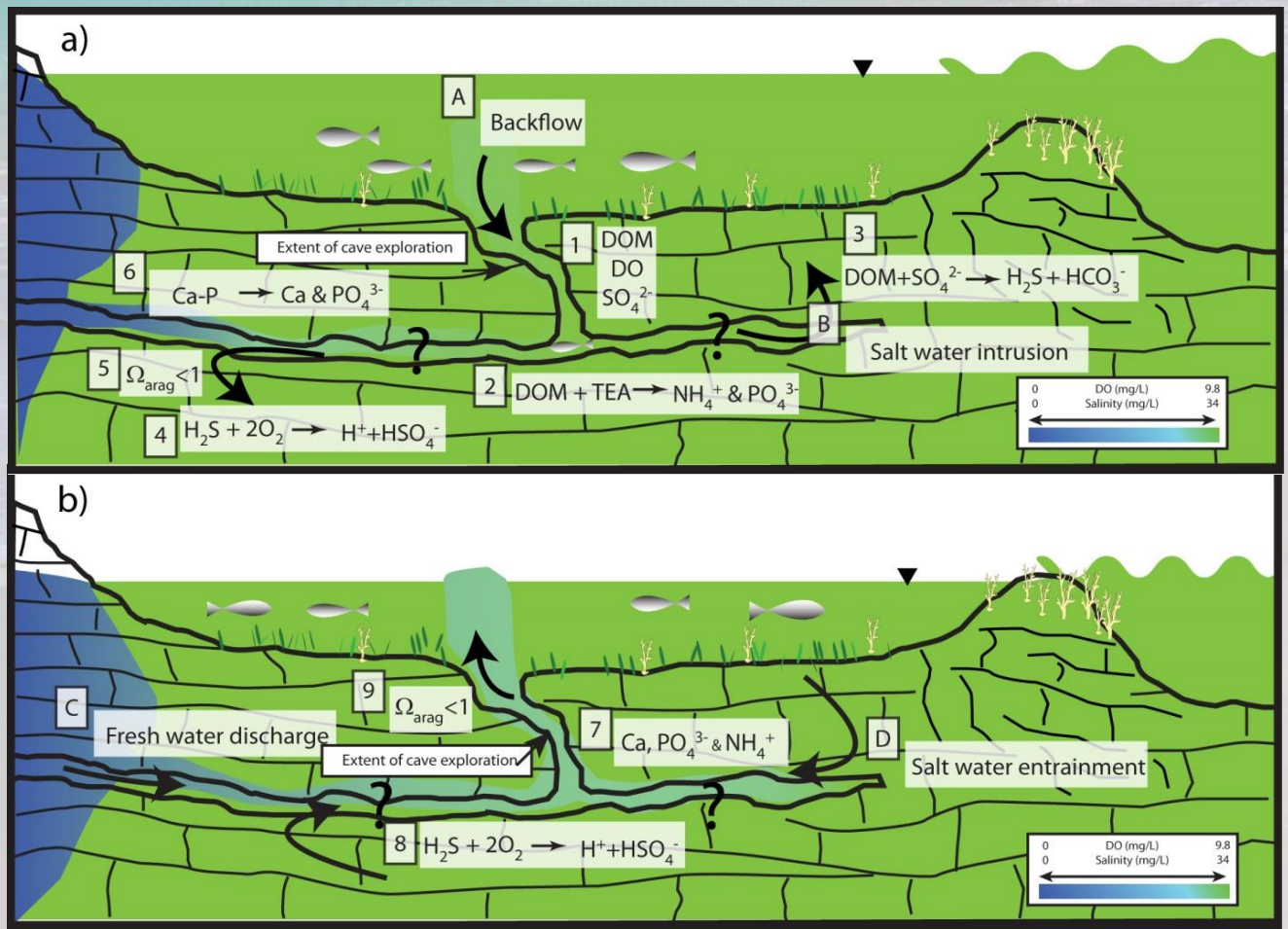
- DO and pH vary with recharge/discharge cycle
  - OC and sulfide oxidation → decrease pH → dissolve calcite
  - Release nutrient from OC (N and P)
  - Release P from calcite surfaces



Young et al., in review

Summary - reefs

- Sulfide-rich and low pH water discharge may degrade corals & seagrasses
- Elevated natural nutrient discharge may enhance corals and seagrasses
- Sea level change will shift distribution of discharge points



Young et al., in review

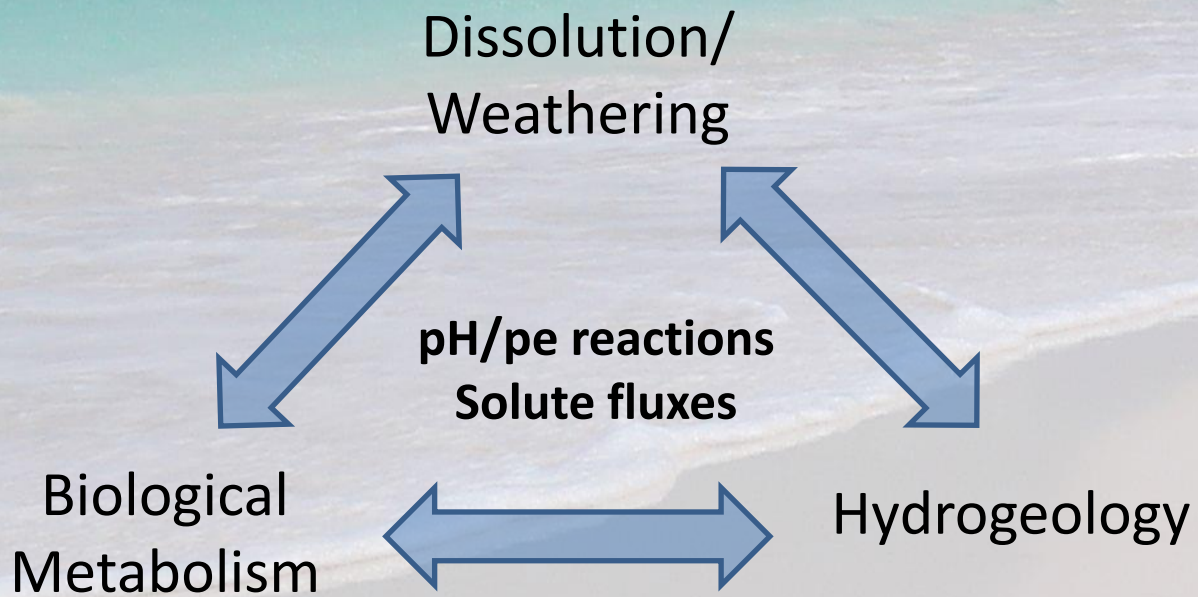
Conclusions

- Don’t forget about carbonate!!
- Solubility → voids not regolith formed
  - Dissolution linked to photosynthesis & respiration & hydrology
  - Even though only voids remain, impacts solute fluxes
    - importantly C, N and P fluxes
  - Solutes important for ecosystem services

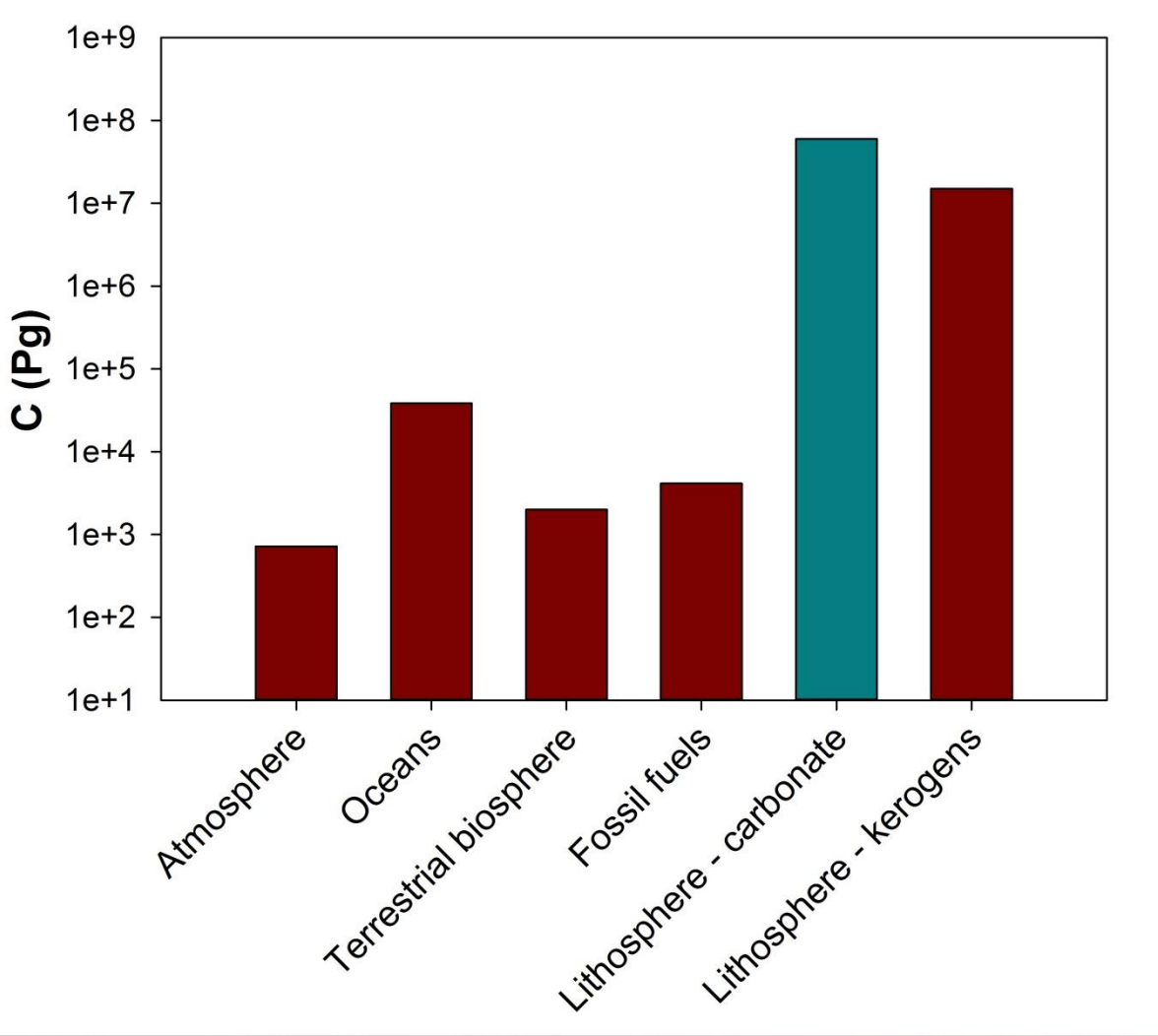
- Also important →

Conclusions

Don’t forget about carbonate!!



Earth's C Reservoirs



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  - ~10^8 Pg
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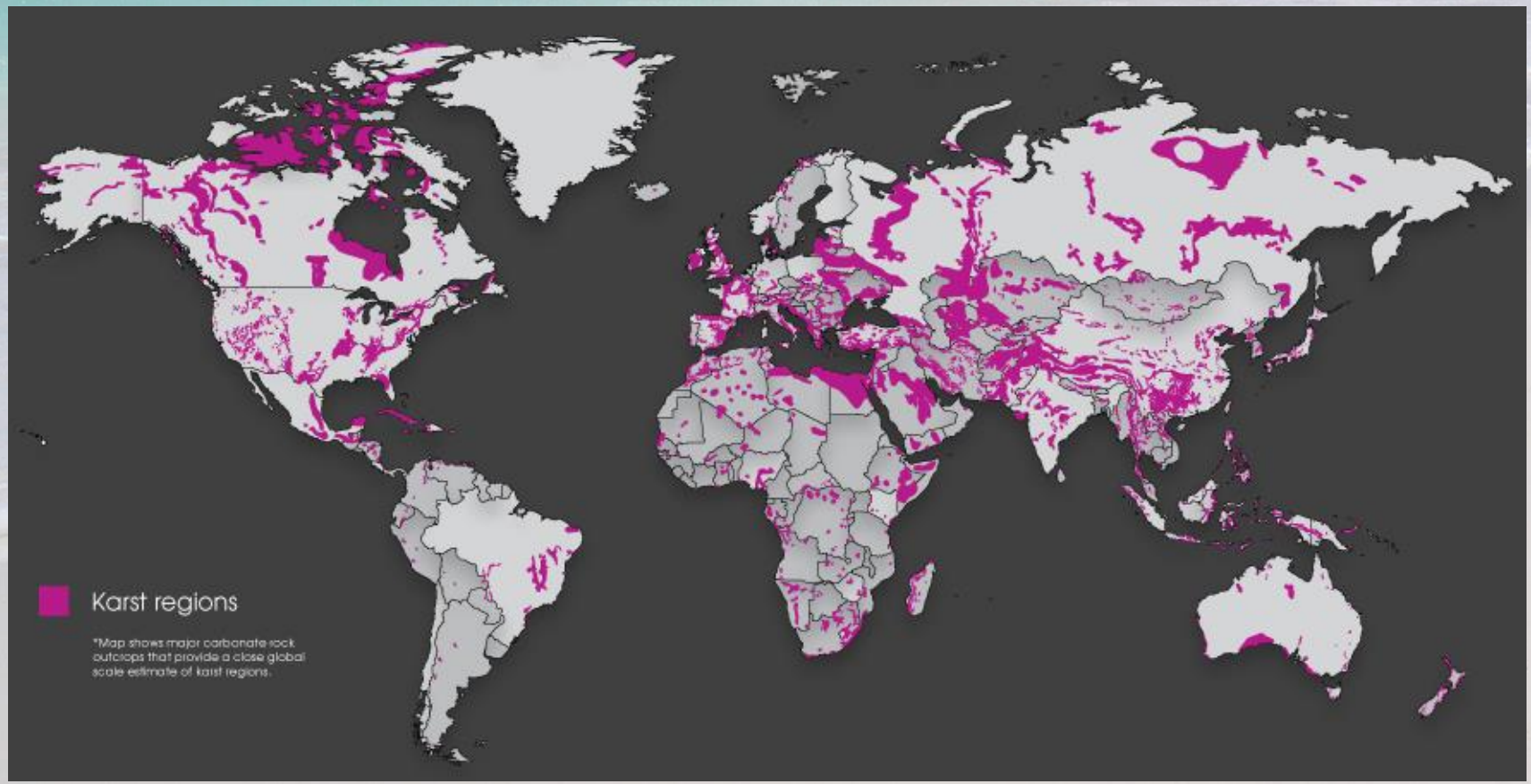
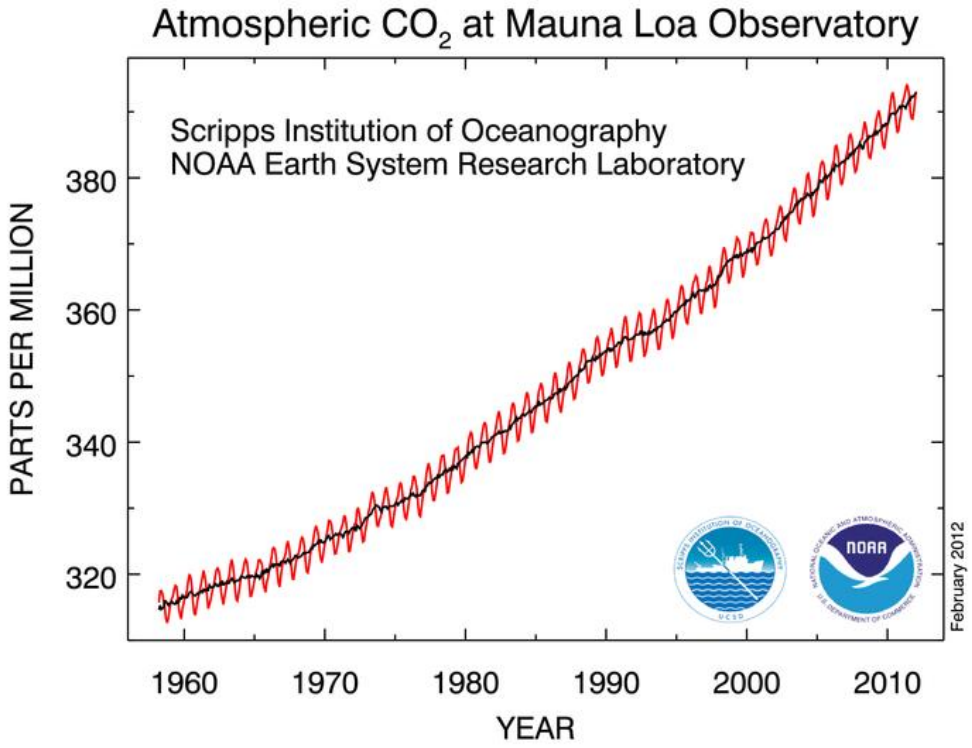
Data from Falkowski et al., 2000, Science

Surface Distribution of Carbonates

- Carbonates cover ~ 20% of ice-free Earth surface
- Weathering of these carbonate minerals are part of global C cycle

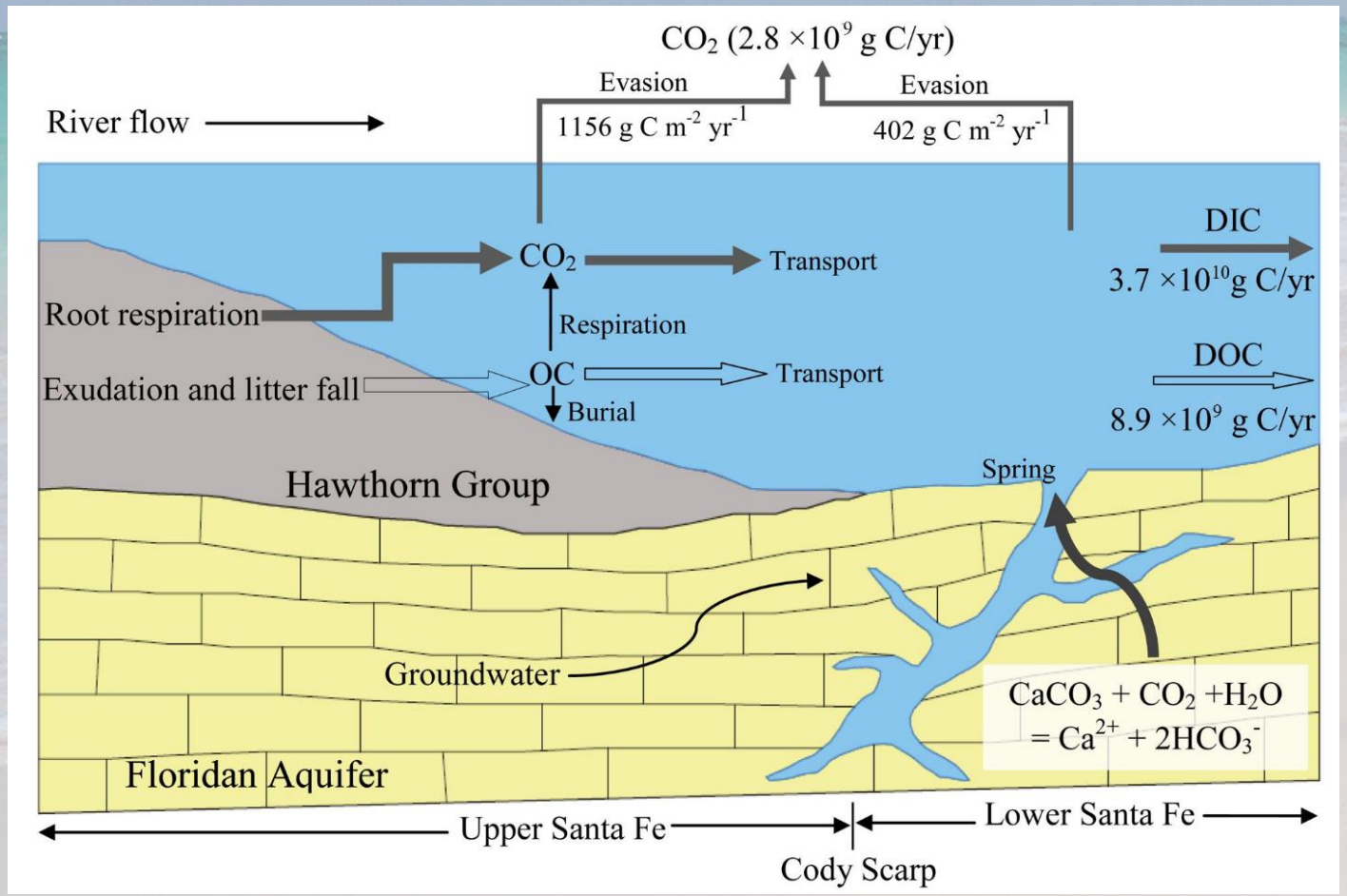


Atmospheric CO_2



Keeling Curve

- Measured increase in atmospheric CO_2 concentrations 1957-2011
- Fossil fuel combustion, deforestation, cement production
- What are impacts on Earth's environments?


CO_2 (2.8 ×10^9 g C/yr)
Evasion
1156 g C m^{-2} yr^{-1}
Evasion
402 g C m^{-2} yr^{-1}
River flow
CO_2
Transport
DIC
3.7 ×10^{10}g C/yr
Root respiration
Respiration
OC
Transport
DOC
Exudation and litter fall
Burial
8.9 ×10^9 g C/yr
Hawthorn Group
Spring
Groundwater
$CaCO_3 + CO_2 + H_2O = Ca^{2+} + 2HCO_3^-$
Floridan Aquifer
Upper Santa Fe
Lower Santa Fe
Cody Scarp