Weathering in modern carbonate terrains

Biological controls on redox condition, dissolution and atmospheric CO_2 fluxes

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Funding

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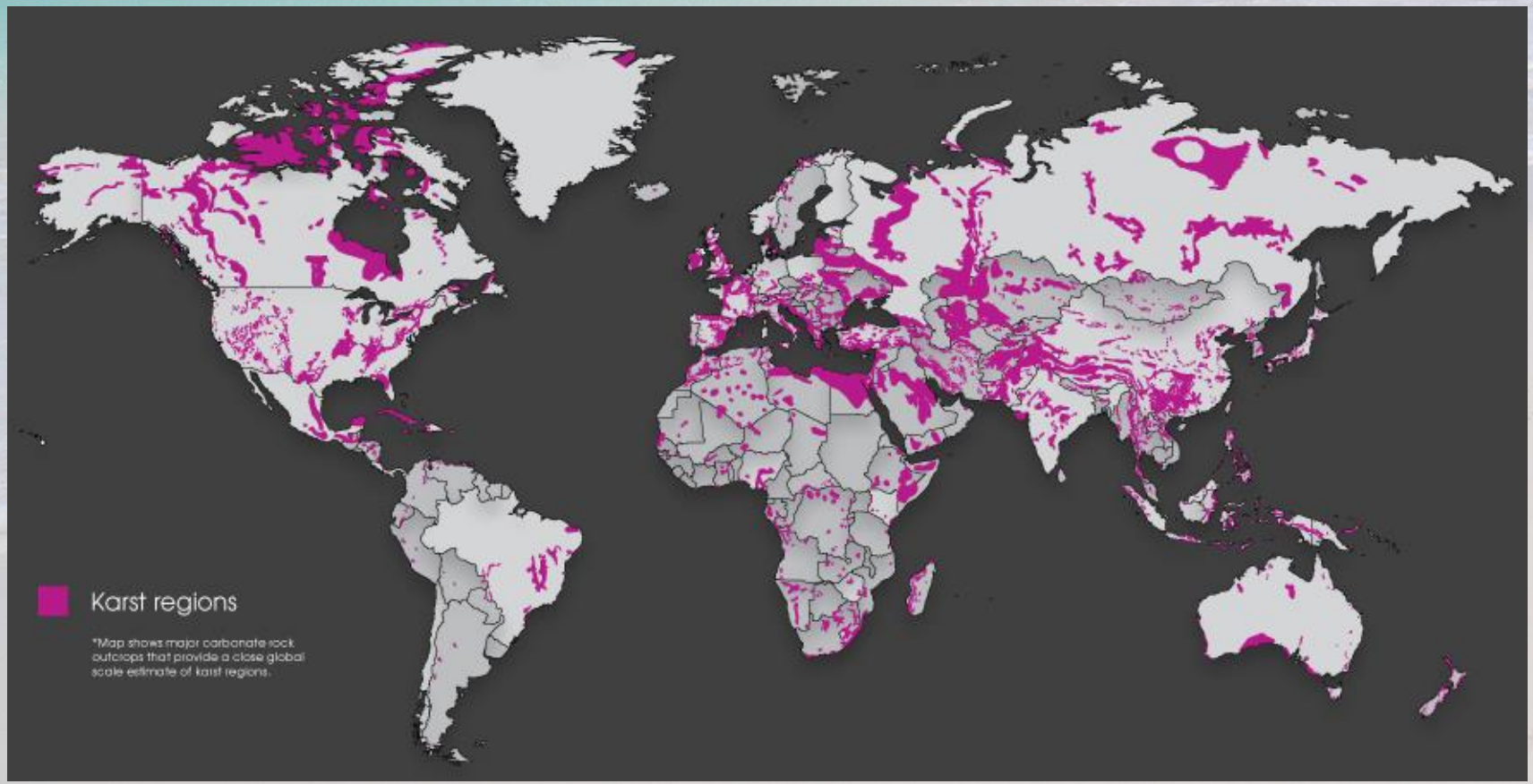
Global Distribution of Carbonates

- Carbonates cover ~ 20% of ice-free Earth surface; largest global reservoir of C:
  - ~10^8 Pg vs ~$5x10^4$ (ocean) & ~10^3 (atmosphere)
- Weathering differs from silicate systems:
  - Congruent versus incongruent dissolution $\rightarrow$ Void spaces versus regolith



Controls on Dissolution

Largely from microbial and plant metabolism

Redox: OC oxidation with TEAs (DO, NO_3, Fe- & Mn-Oxides, SO_4)

Acid dissolution: H_2CO_3; H_2SO_4

Fracture and water table caves, Florida

Lake George Blue Hole
Rum Cay, Bahamas

Angelita Cenote
Quintana Roo, Mexico

Significance of different acids

- **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

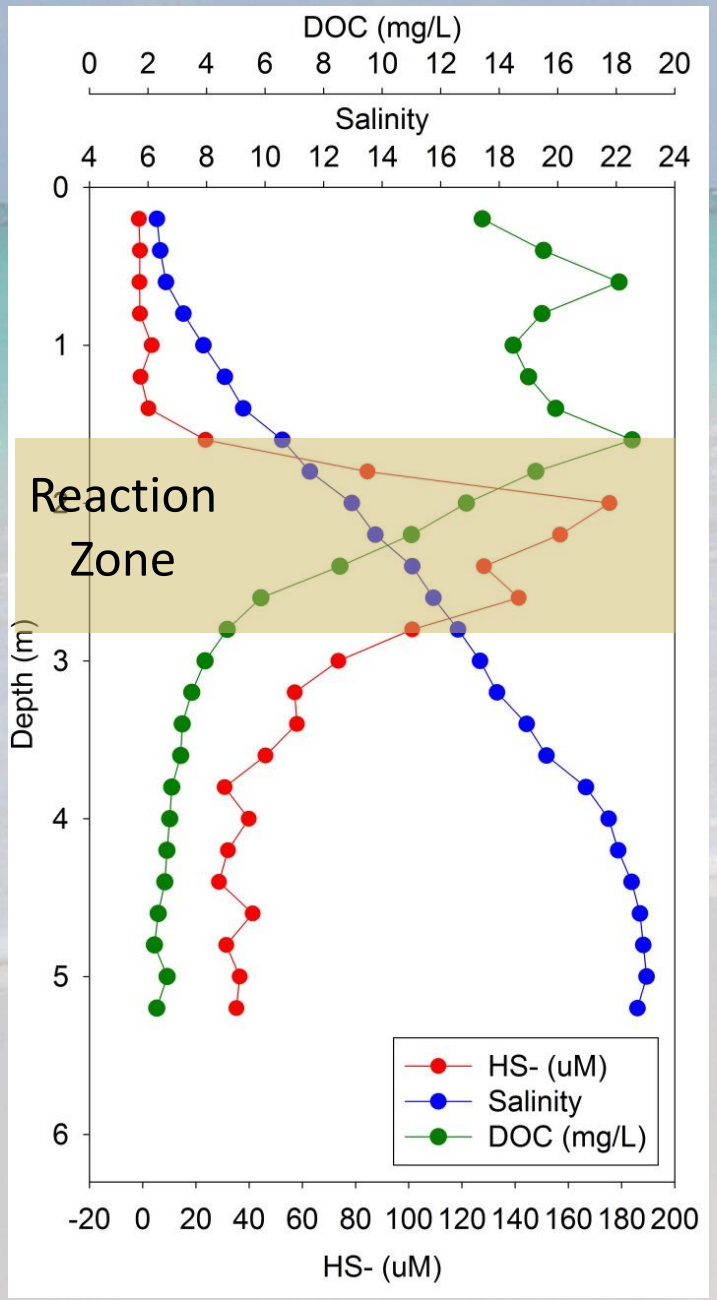
- **Sulfuric acid dissolution:**

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

  - Net CO_2 source to atmosphere

- **Today – some examples**

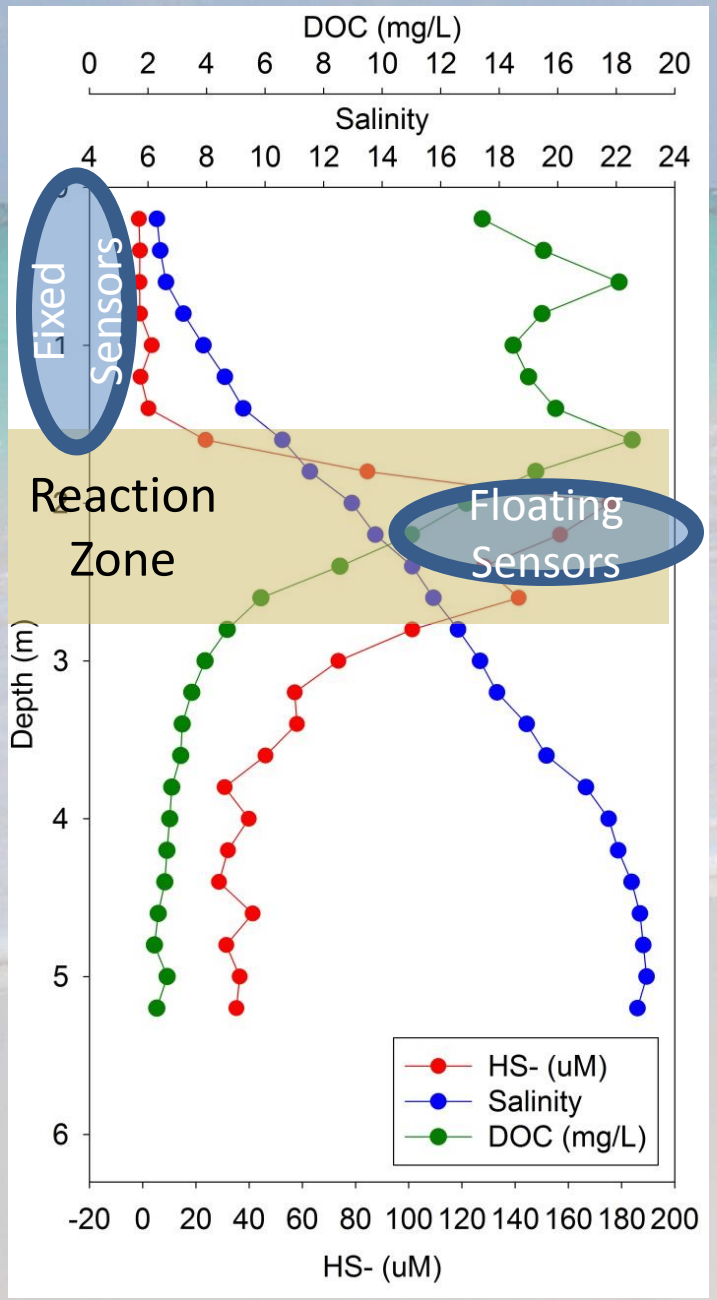
Ink Well Blue Hole, Bahamas



- 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

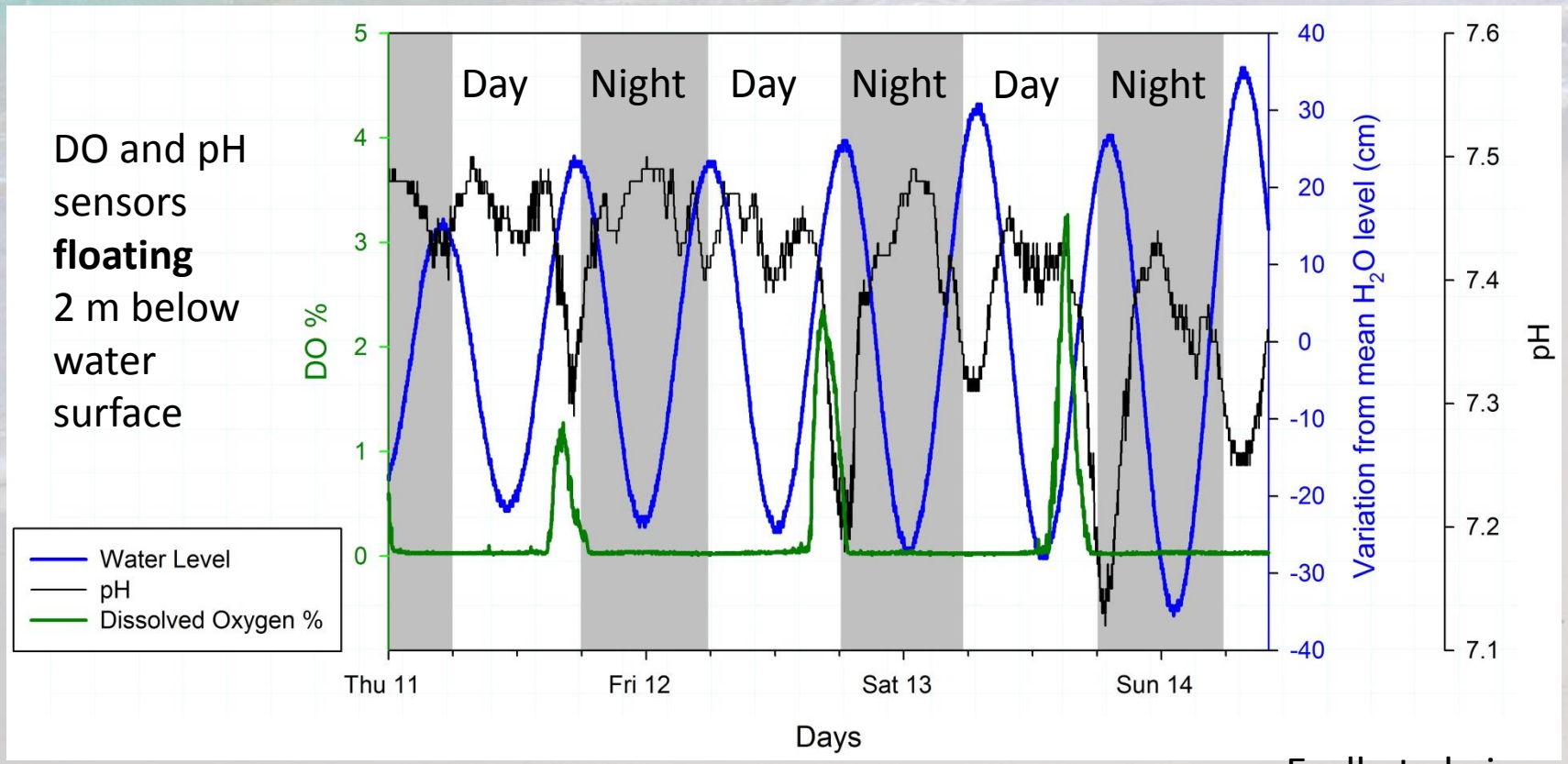


- Is system static or dynamic?
- San Salvador Island
  - Small (~50 km^2) island
  - Isolated platform
- At pycnocline/halocline:
  - Organic carbon trapped
  - Sulfate reduction increases sulfide concentrations
  - Sulfide oxidized as diffuses upward to oxic
  - Decreases pH

Pain et al., in prep.

Dynamics at pycnocline

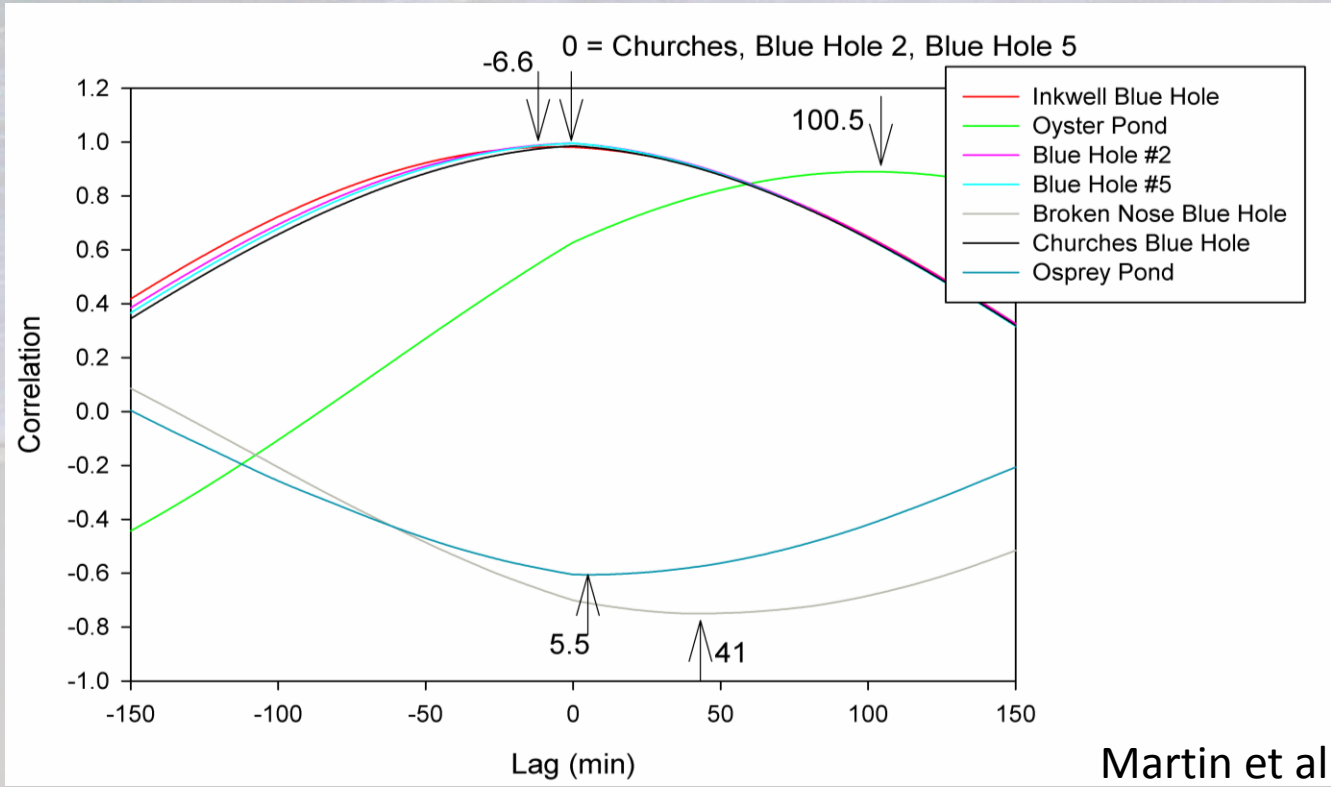
- Low tide increase radiation and photosynthetic DO production
- pH drops follows DO production – DO consumption and sulfide oxidation
- Does low pH water exchange with aquifer? What causes head gradient?



Ezell et al., in prep.

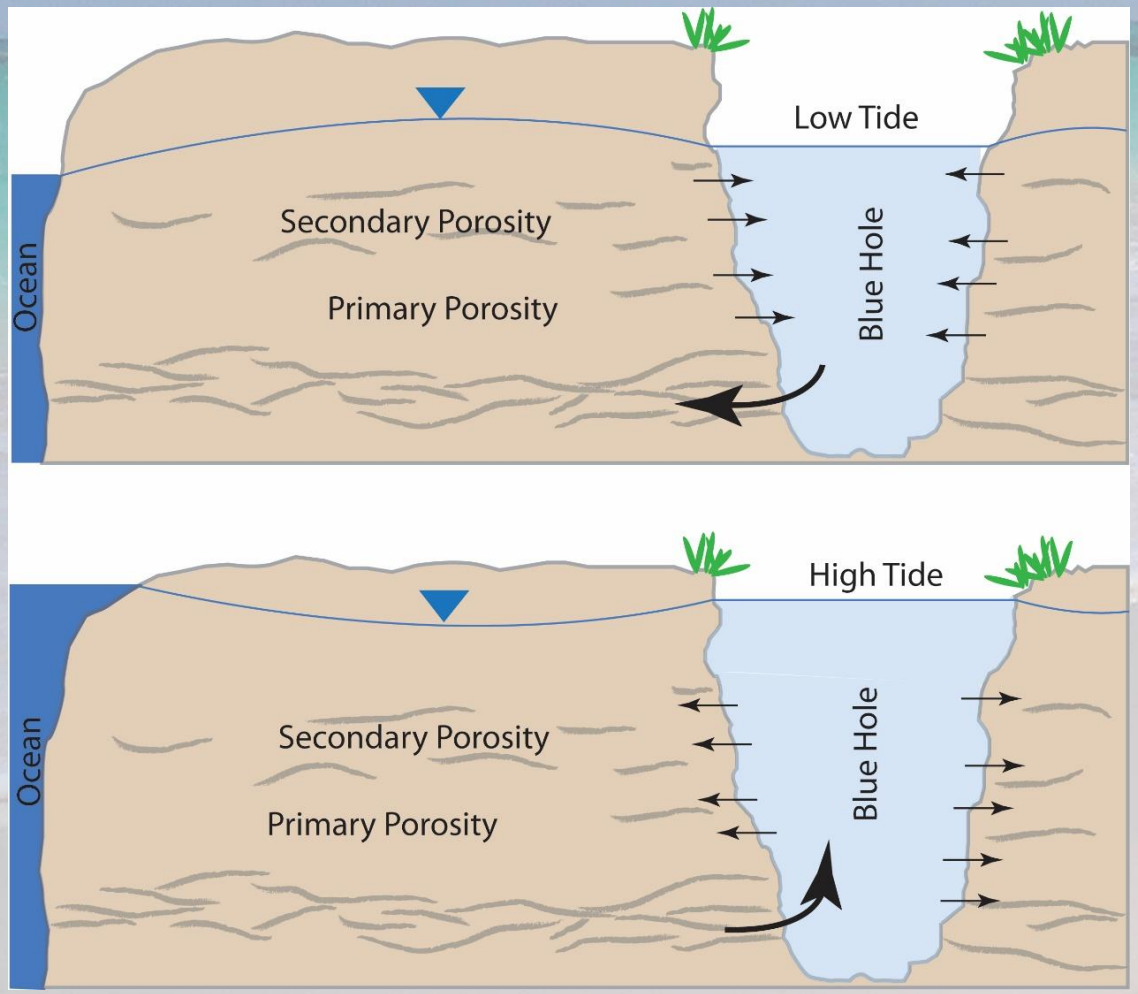
Lags between inland water and ocean

- 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



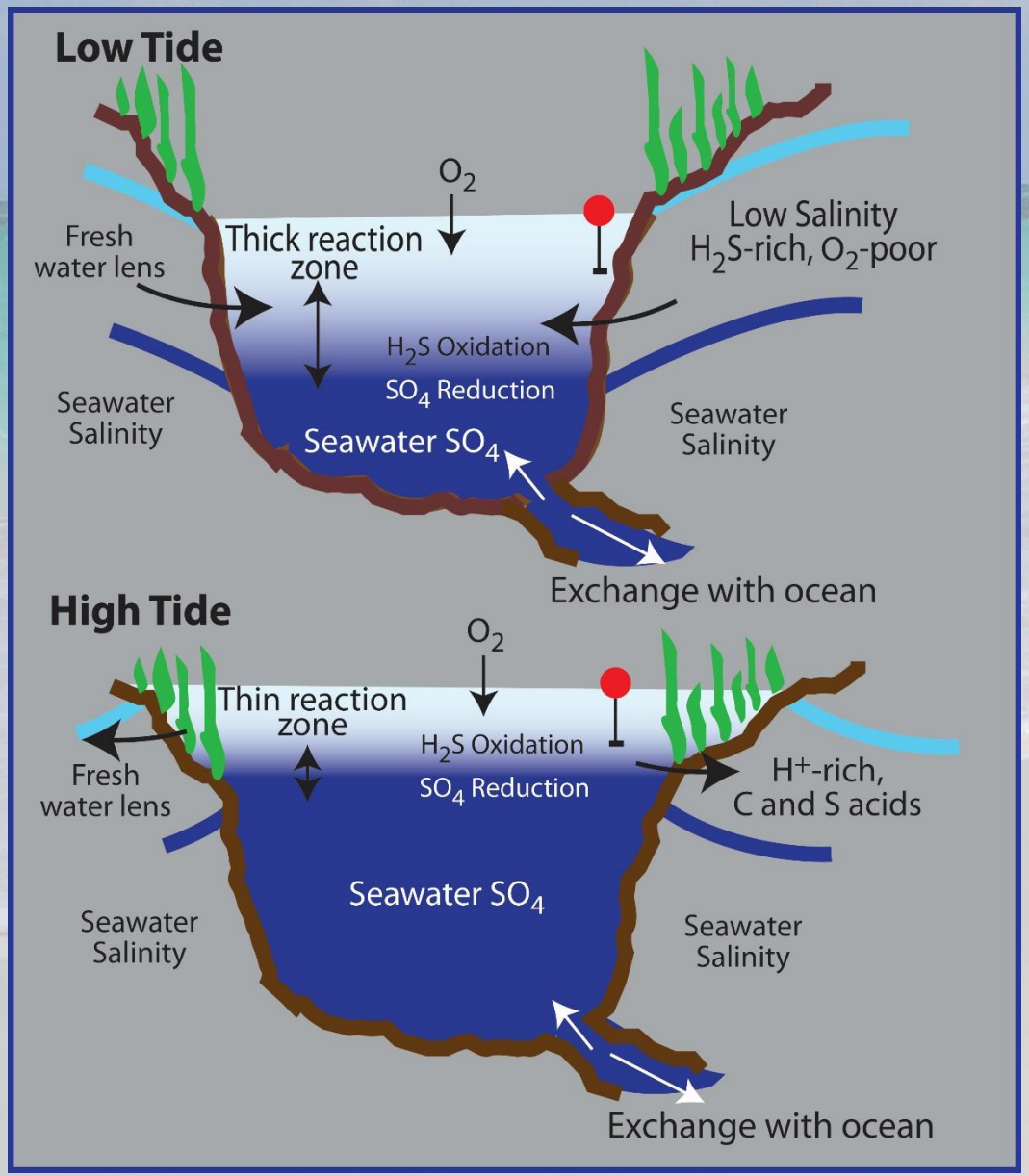
Martin et al., 2012 J Hydro

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

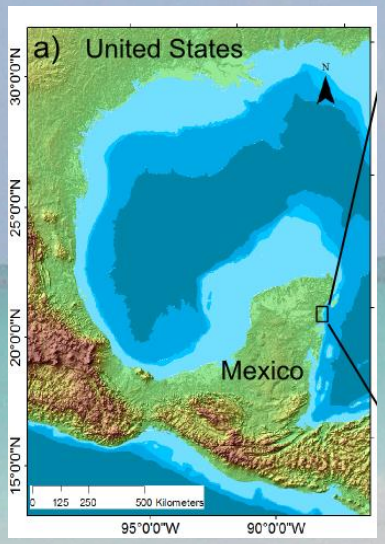
Martin et al., 2012 J Hydro

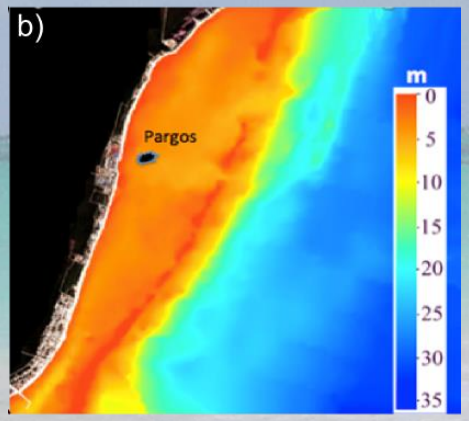


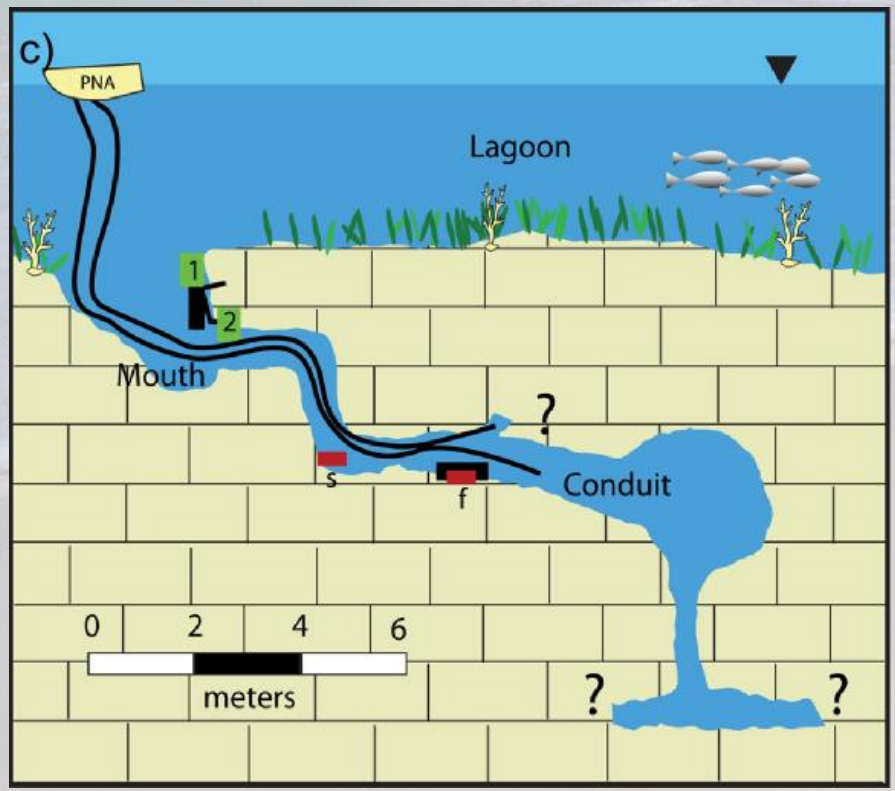
Summary

- 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





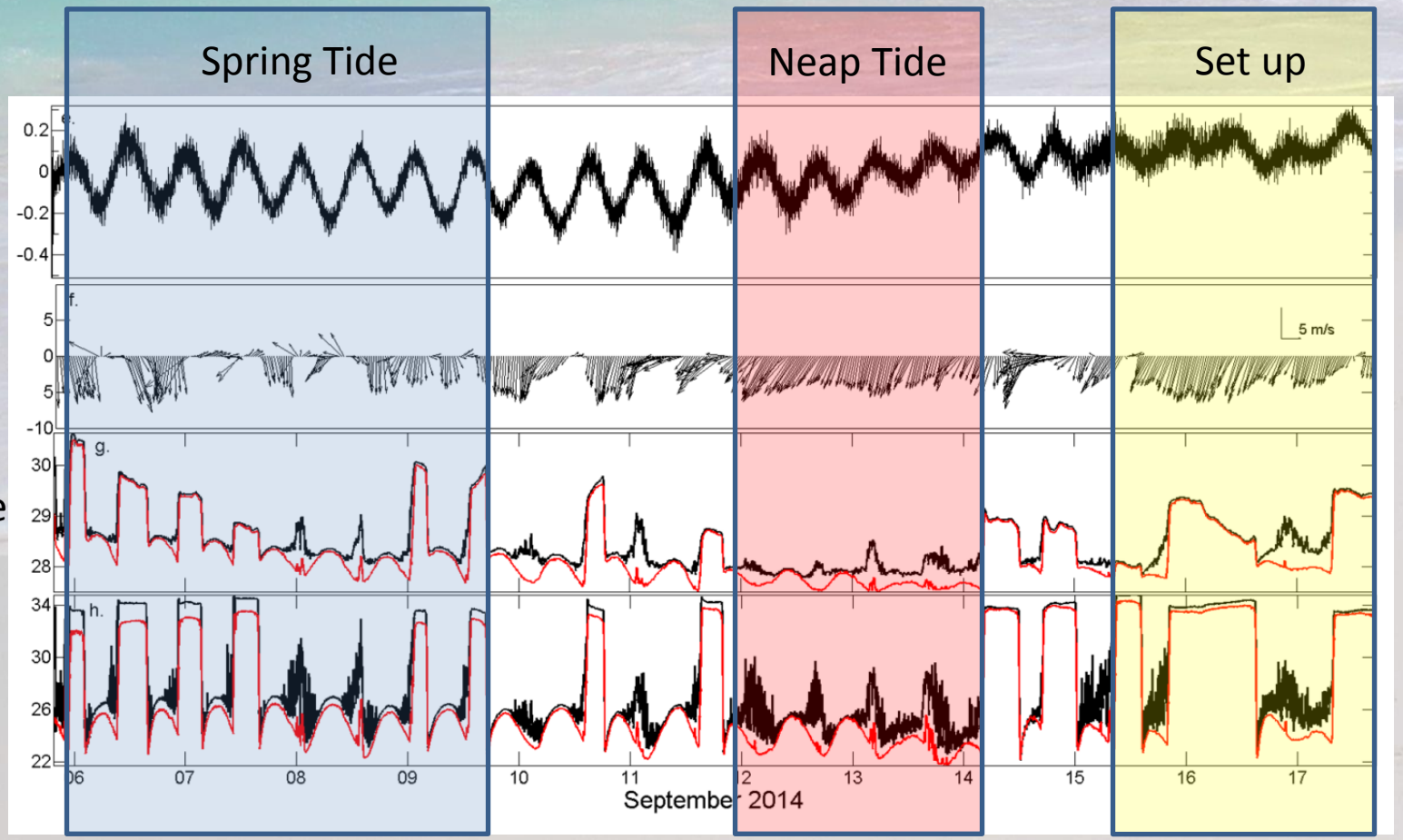


- Cave system offshore Yucatan Peninsula
- No surface drainage to oceans
- Multiple springs including Pargos Spring:
  - Cave exploration and instrumentation within cave and lagoon
  - Grab samples from within cave and lagoon

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

Two week time series

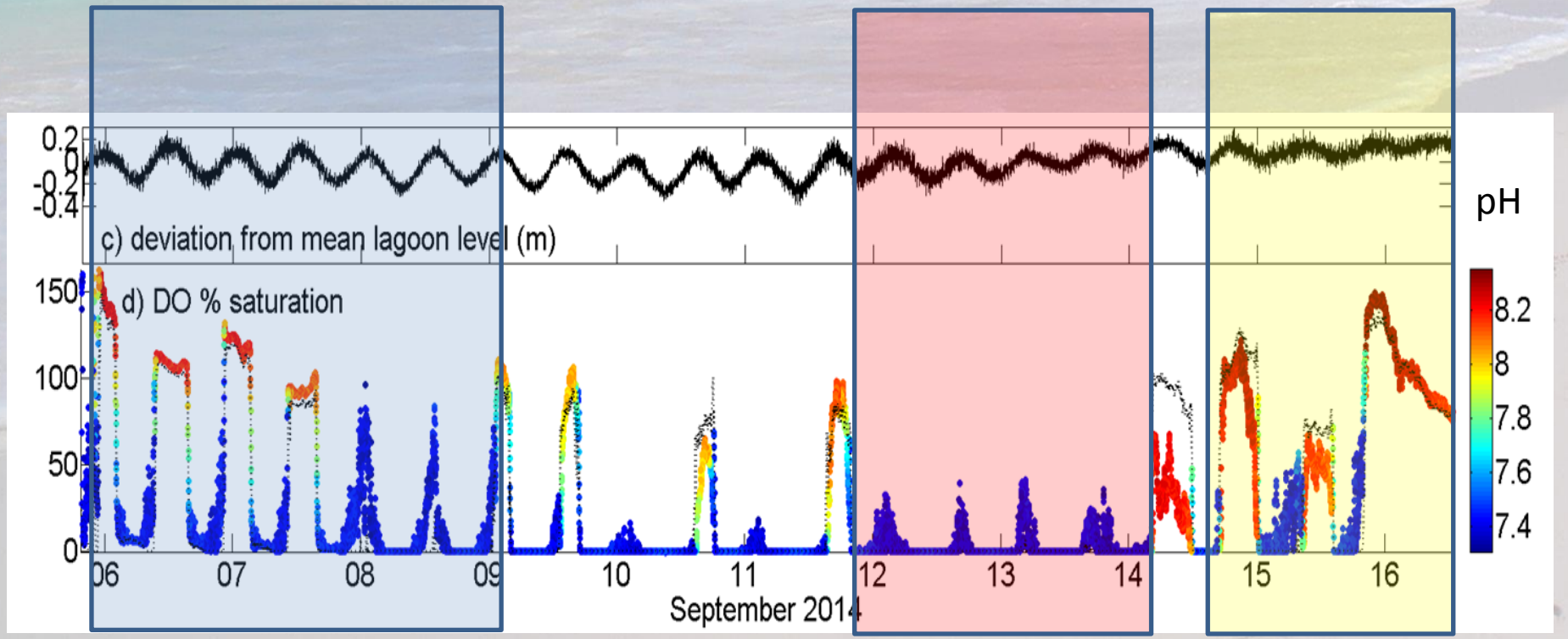
- T and S show reversing flow at spring
- Reversal frequency controlled by tides (spring/neap) and winds
  - Discharge when SL < 8 cm above average
  - Recharge when SL > 8 cm above average (20 – 30 yr SLR)



Young et al., in review

Reactive components

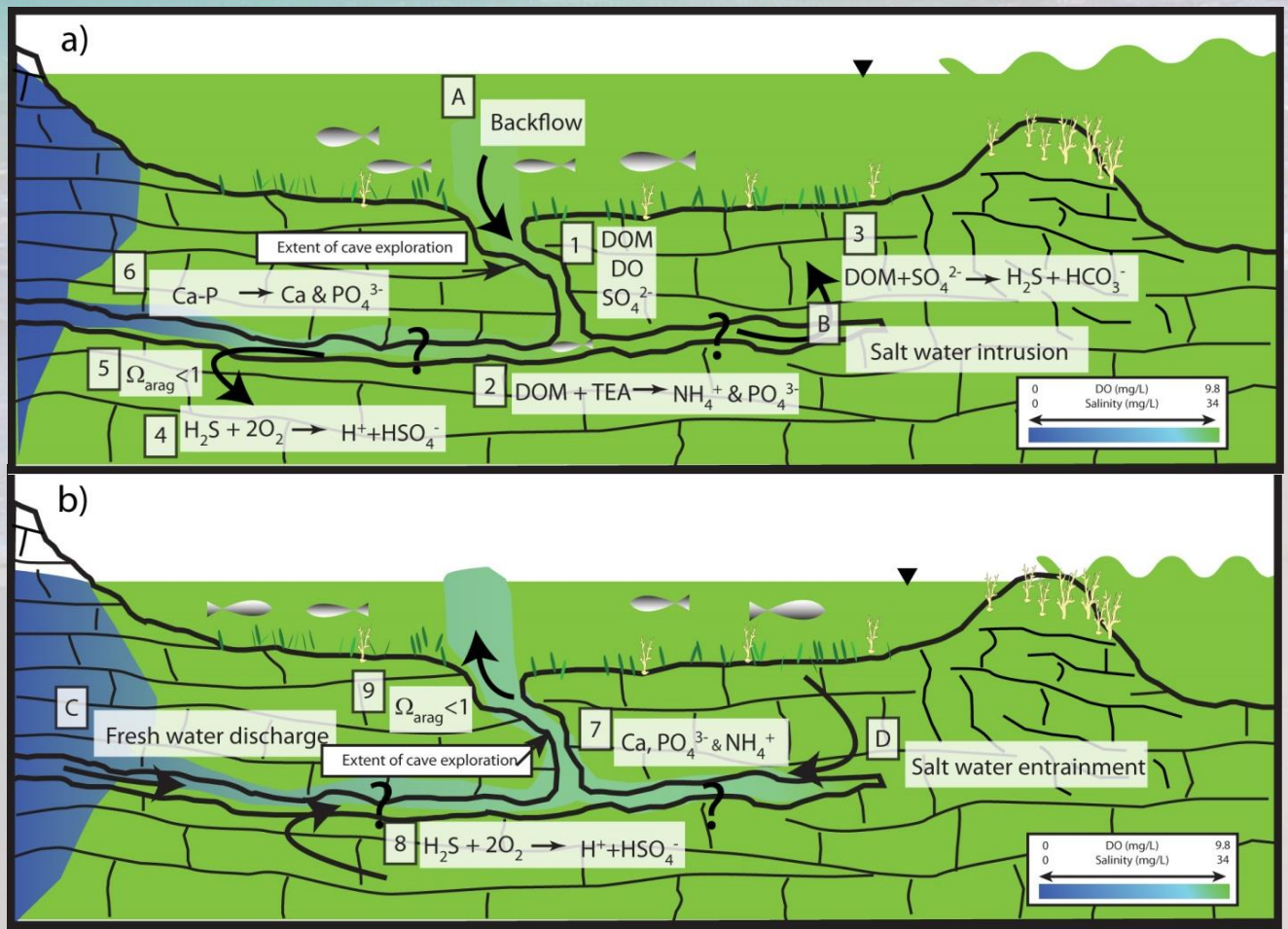
- DO and pH vary with recharge/discharge cycle
  - OC and sulfide oxidation → decrease pH → dissolve calcite
  - Release nutrient from OC (N and P)
  - Release P from calcite surfaces



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!!