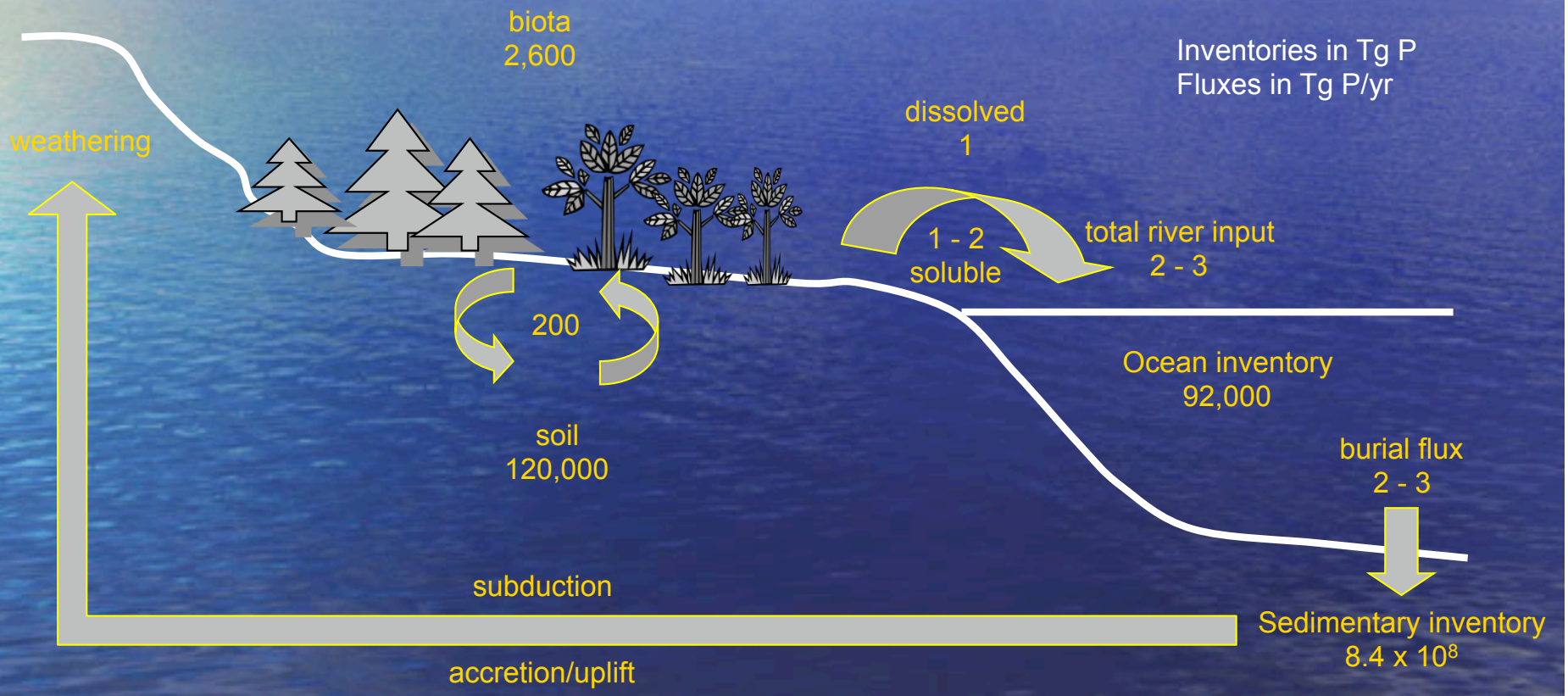
Marine P cycling

- What we know about water column dynamics
- What we know about P sedimentation
- What we are thinking about the marine P mass balance and geological variations in the P cycle
- What we have little/no clue about
  - Terrestrial weathering dynamics
  - Link between P, C, oxygenation, ocean ecosystem structure
  - P cycling at the advent of "rootedness"

Reservoirs and fluxes

Natural (pre-human) dissolved phosphorus cycle



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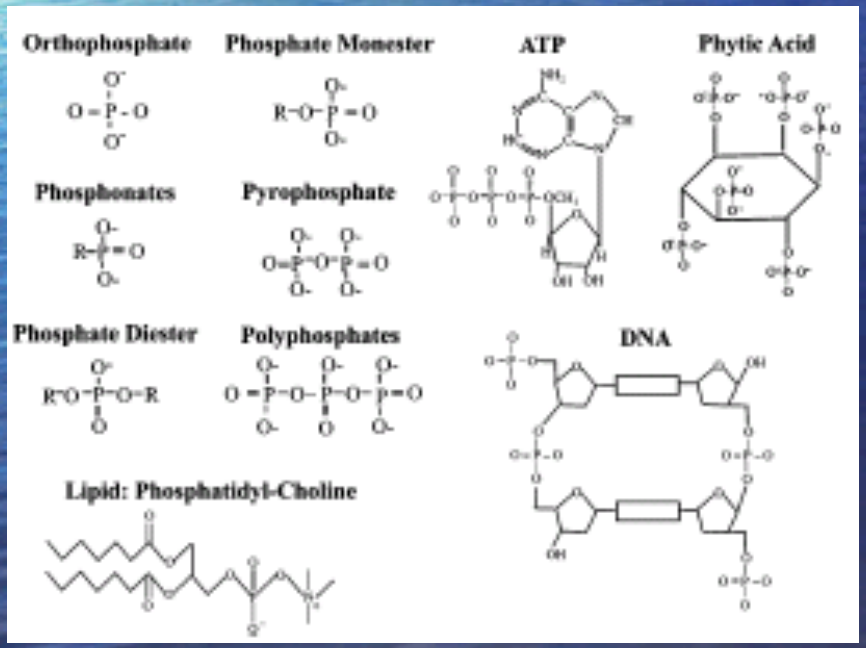
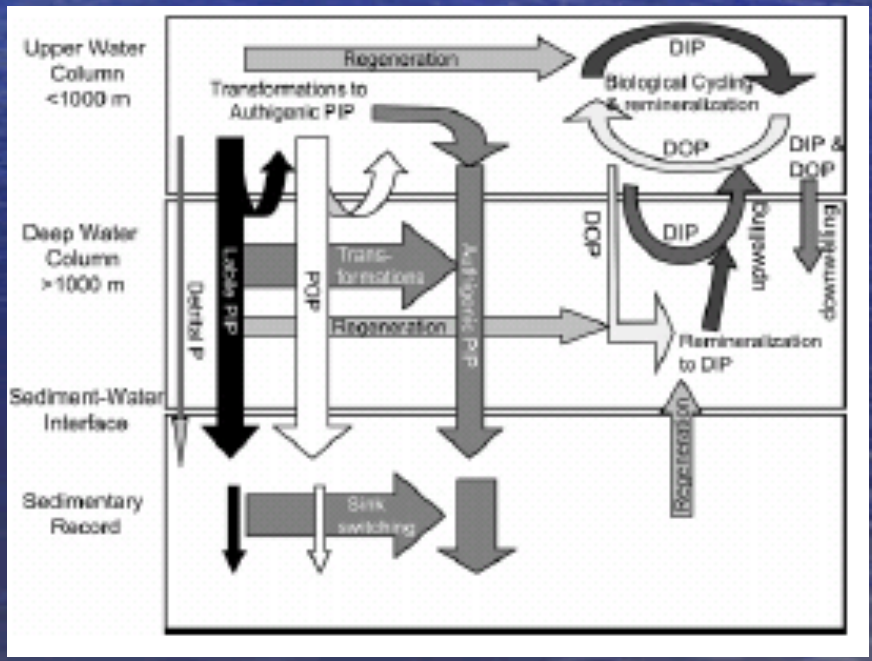
Marine P chemistry

- The role of organic-P complexes; phosphonate production in oligotrophic regions; microbial links between N and P





Marine P chemistry

- Modern P limitation in the ocean
  - Open ocean
    - Recycling efficiency >99%
  - Freshwater-dominated coastal environments
    - Surface ocean [P] much lower than riverine
  - P the geologically limiting nutrient
    - Nitrogen important on daily to annual timescales, but huge atmospheric pool
    - Silica, Iron, important but spatially/ecologically limited

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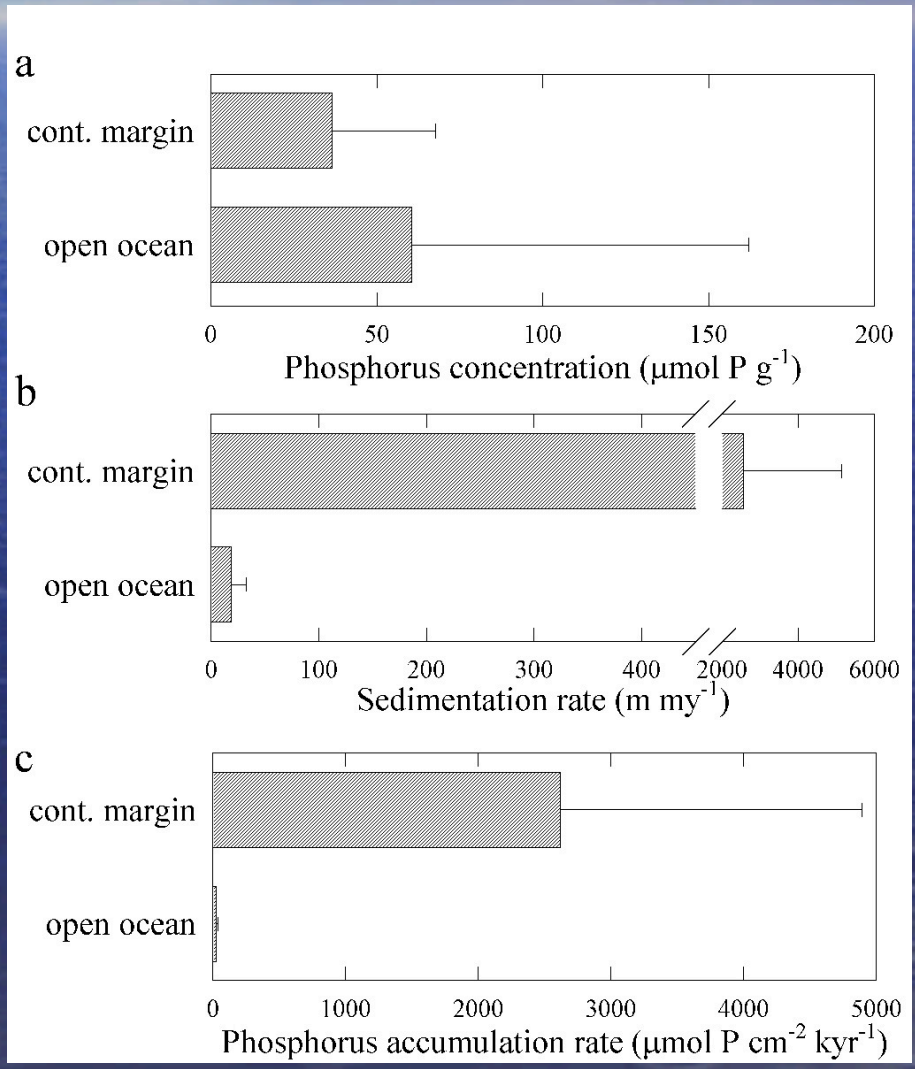
What we have learned about sedimentary P geochemistry

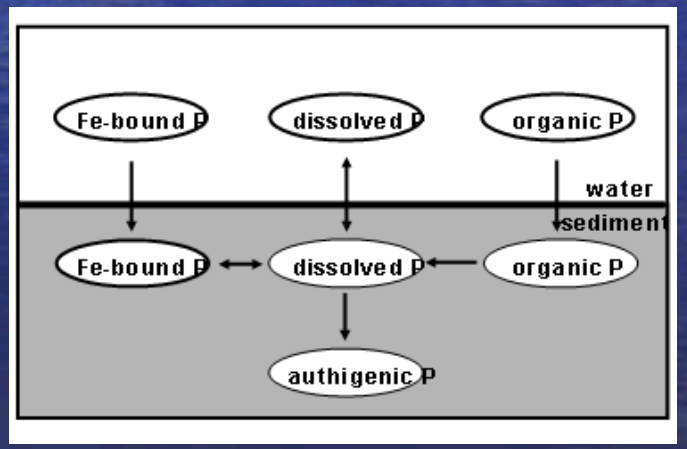
- Modern continental margin sink is about 50% of global ocean sink
- Sedimentation rate differences are key, with phosphorus recycling back to the water column inversely correlated with sedimentation rate



Sedimentation sequestration of marine P

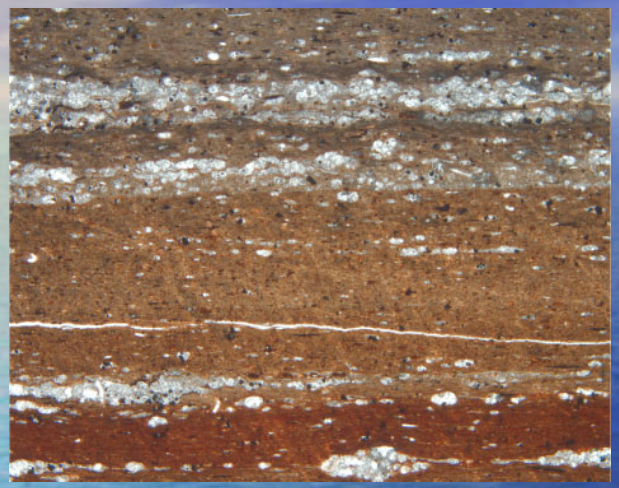
Phosphogenesis: A biogeochemical process

- Formation of authigenic phosphate minerals—in marine settings, usually Carbonate Fluorapatite (CFA)
- Initiated by accumulation of reactive P at the seafloor—requires net P accumulation
- Process involves diagenesis of P-bearing phases, release of P to interstitial waters, and authigenic formation of CFA



- **Where does phosphogenesis occur?**

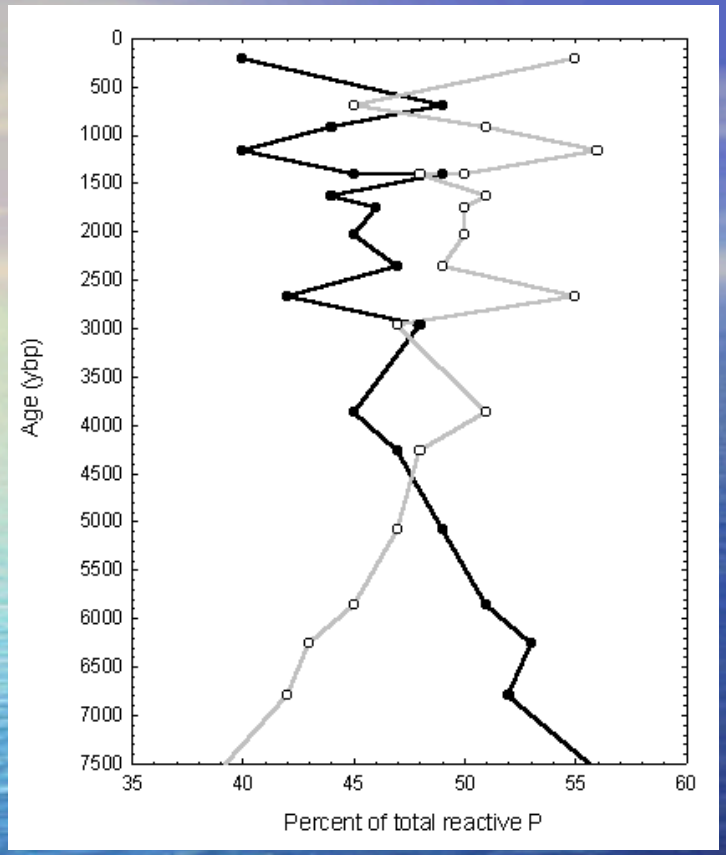
Type-section—phosphatic shales

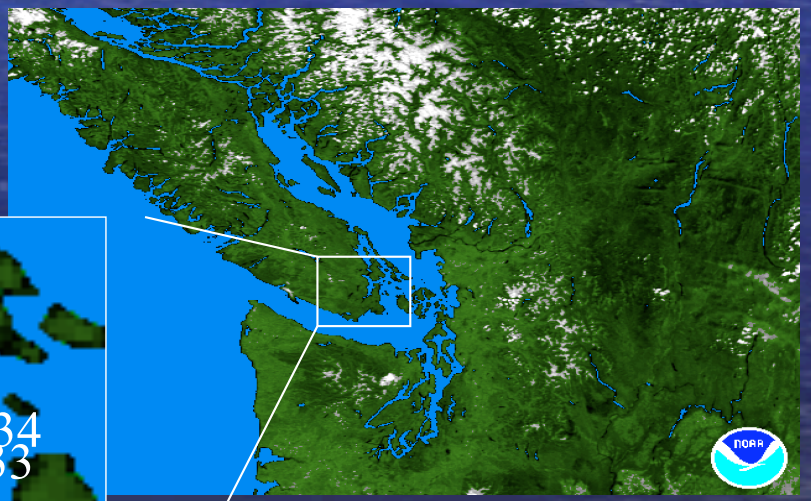


Phosphatic shales Monterey Fm

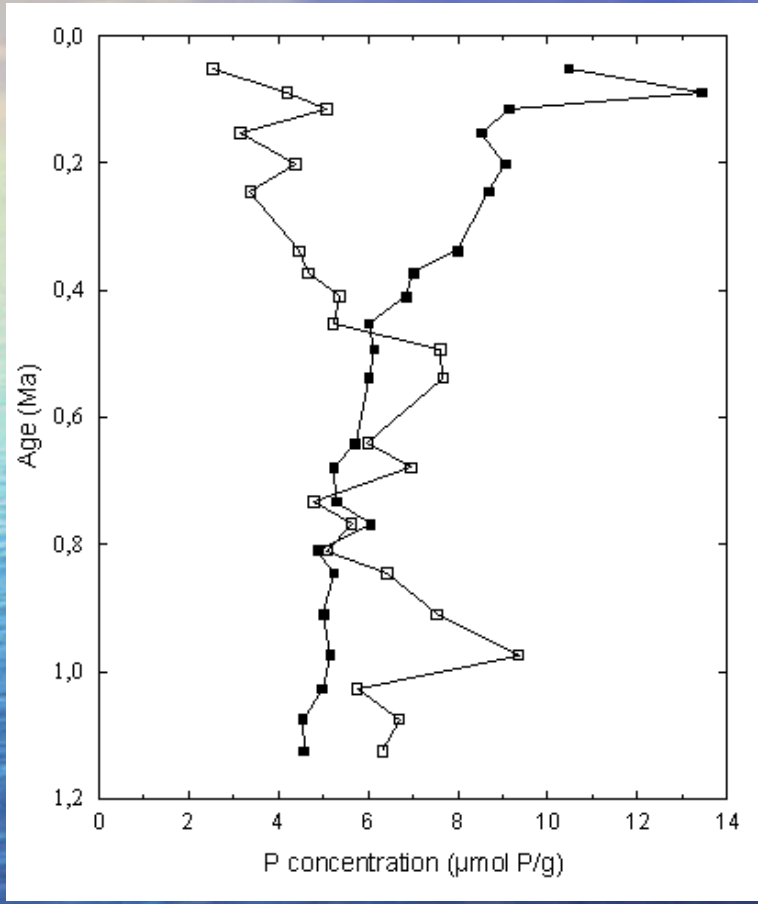
- Phosphatic laminae, micronodules formed by release of P from organic matter and oxides and migration to sites of CFA mineralization
- Controlled by
  - Rate of release
  - Bio-irrigation
  - Permeability
  - Templates for CFA authigenesis
  - Competitive geochemical reactions
- **Where else does phosphogenesis occur?**

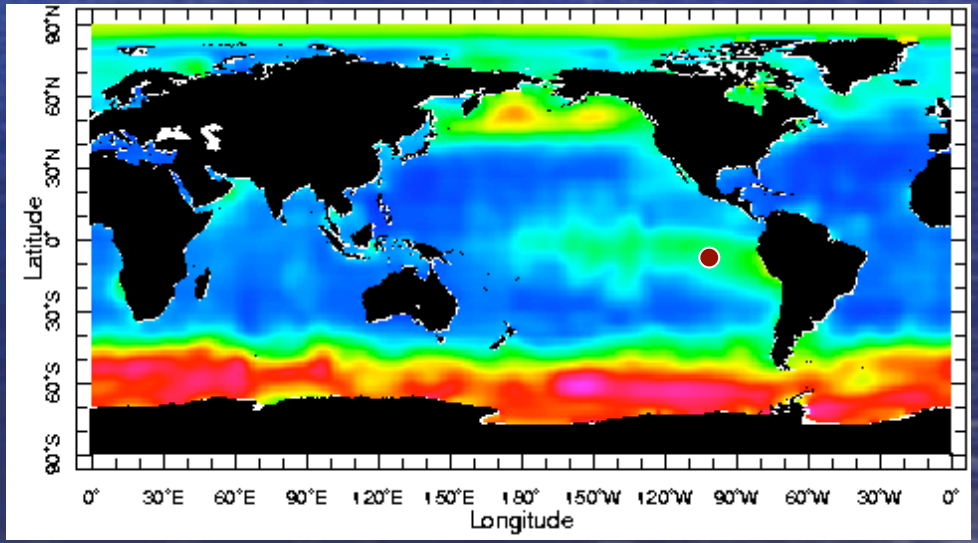
The anoxic Saanich Inlet on timescales of kyrs





the deep eastern equatorial Pacific on timescales of myrs





The ubiquity of phosphogenesis

- The development of more sophisticated P geochemical techniques by a number of researchers around the world has shown the common occurrence of authigenic apatite in many settings
  - although interestingly few studies have tried to "see" disseminated apatite;

- Phosphogenesis is mundane

Marine P cycling

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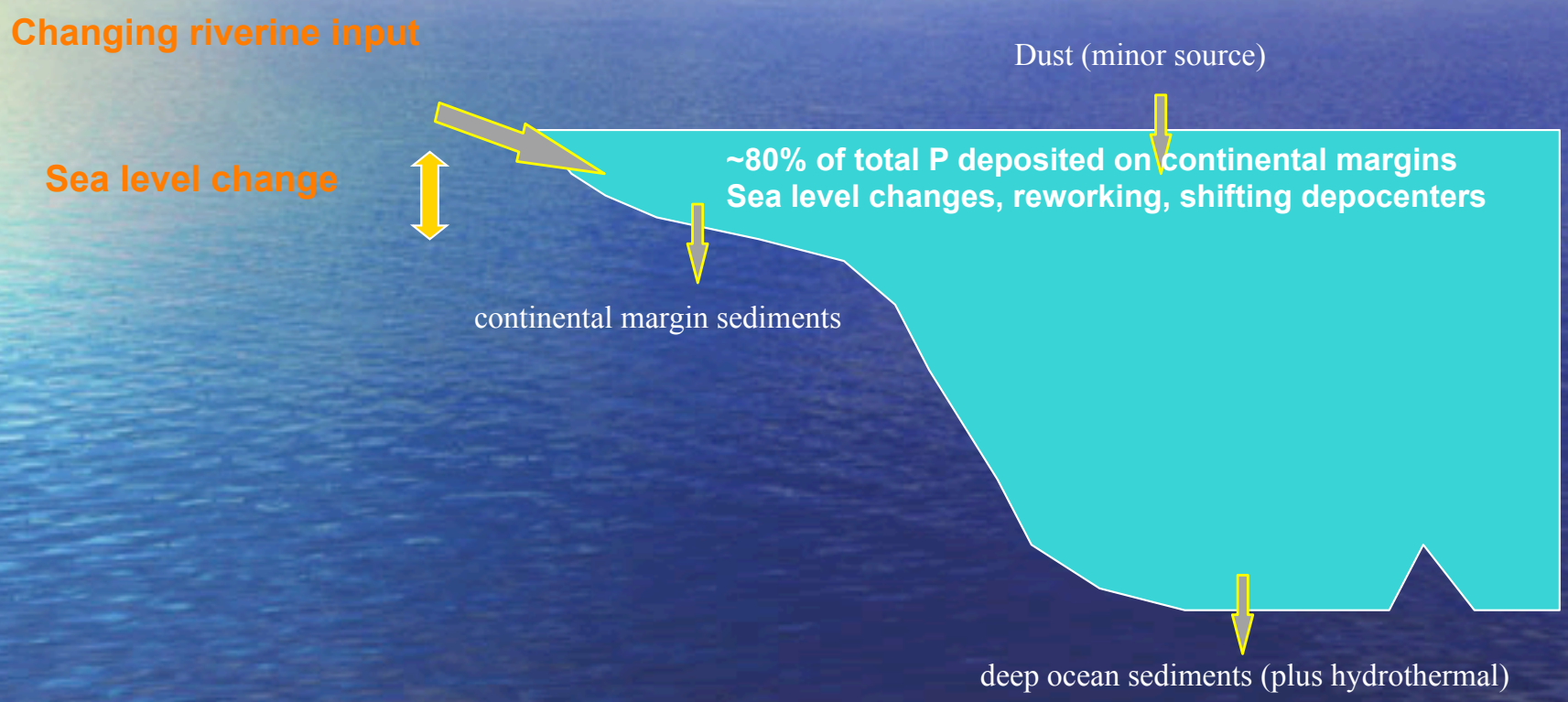
- What we have little/no clue about
  - Terrestrial weathering dynamics (morning/afternoon)
  - Link between P, C, oxygenation, ocean ecosystem structure
  - P cycling in deep time (the advent of "rootedness")

Dynamic phosphorus cycle



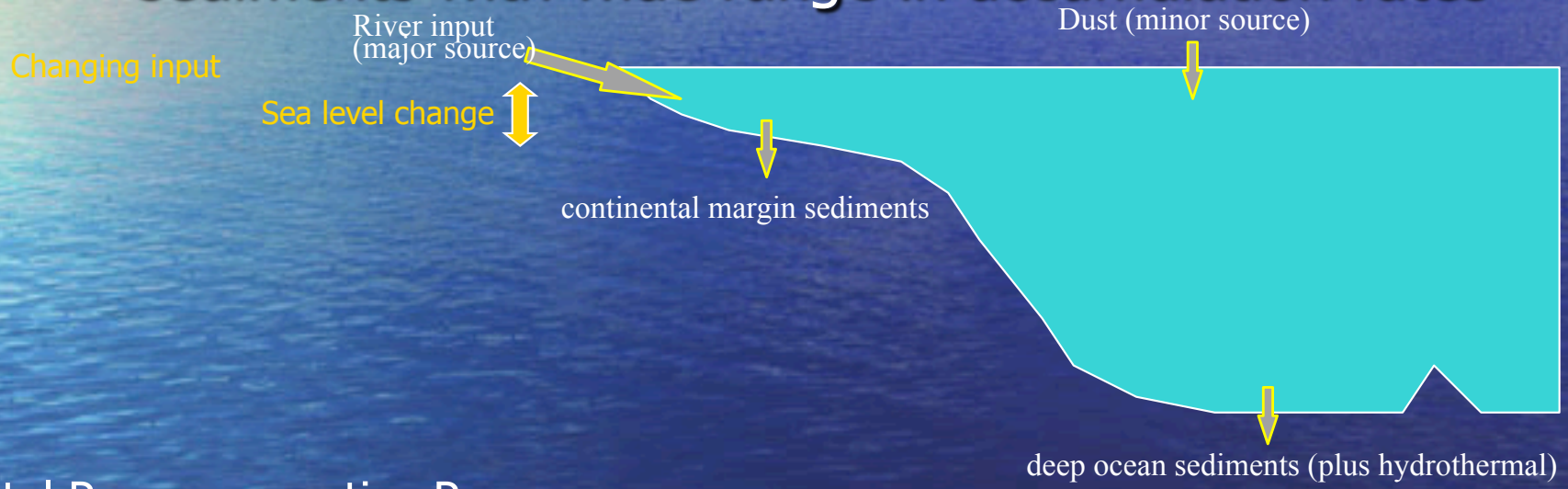
What we are guessing about
Geologic variations in the P cycle

- Attempts to constrain the cycle using mass balance approach
  - would provide the master switch for marine productivity and carbon burial
  - would provide context for weathering release of P from terrestrial systems.

$$\tau_P = \frac{\text{Inventory}}{\text{(input rate) or (output rate)}}$$

Problems with mass balance

- Problem #1—Only integrated record from ocean sediments with wide range in accumulation rates



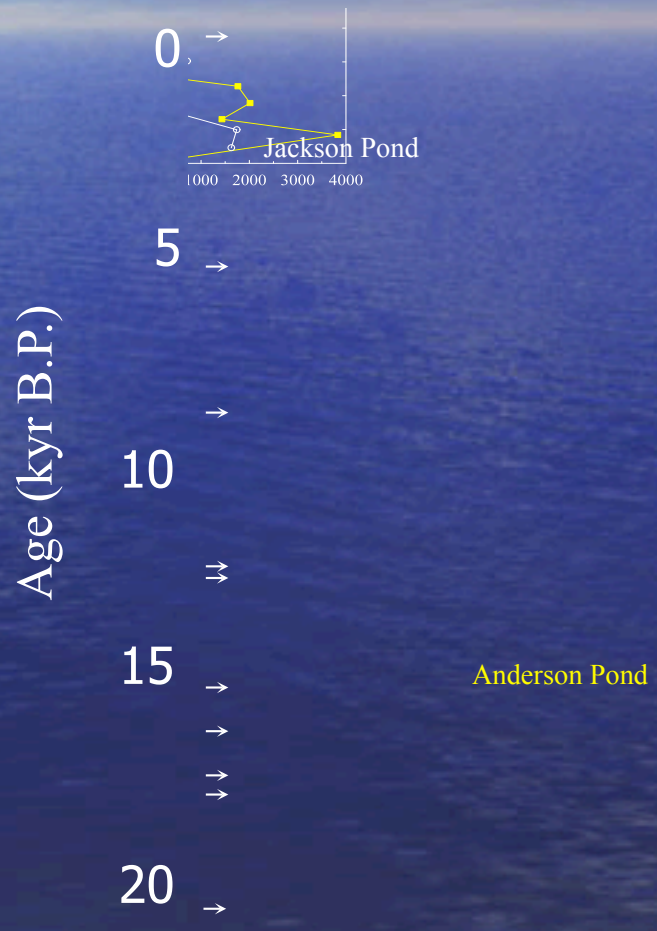
- Total P versus reactive P
- ~80% of total P deposited on continental margins
  - Sea level changes, reworking, shifting depocenters

More problems

- Problem #2—No pre-anthropogenic record of inputs
  - Humans have roughly doubled the input of dissolved phosphorus to the ocean
    - Waste, fertilizers
    - Little is known about particulate phosphorus changes via soil loss, sediment loading of rivers
- Problem #3—Cycle not in steady state
  - Residence time on land
    - ~50 kyr wrt soil and biota
  - Residence time in ocean
    - ~25 kyr wrt sedimentation

What do we know about the terrestrial record? Not much

- Terrestrial P export is very dynamic on G/IG timescales
- Higher rates during glacials and terminations, lower during interglacials when soils reach steady-state conditions
- Caveat—VERY few records



Filippelli and Souch, 1999, Geology

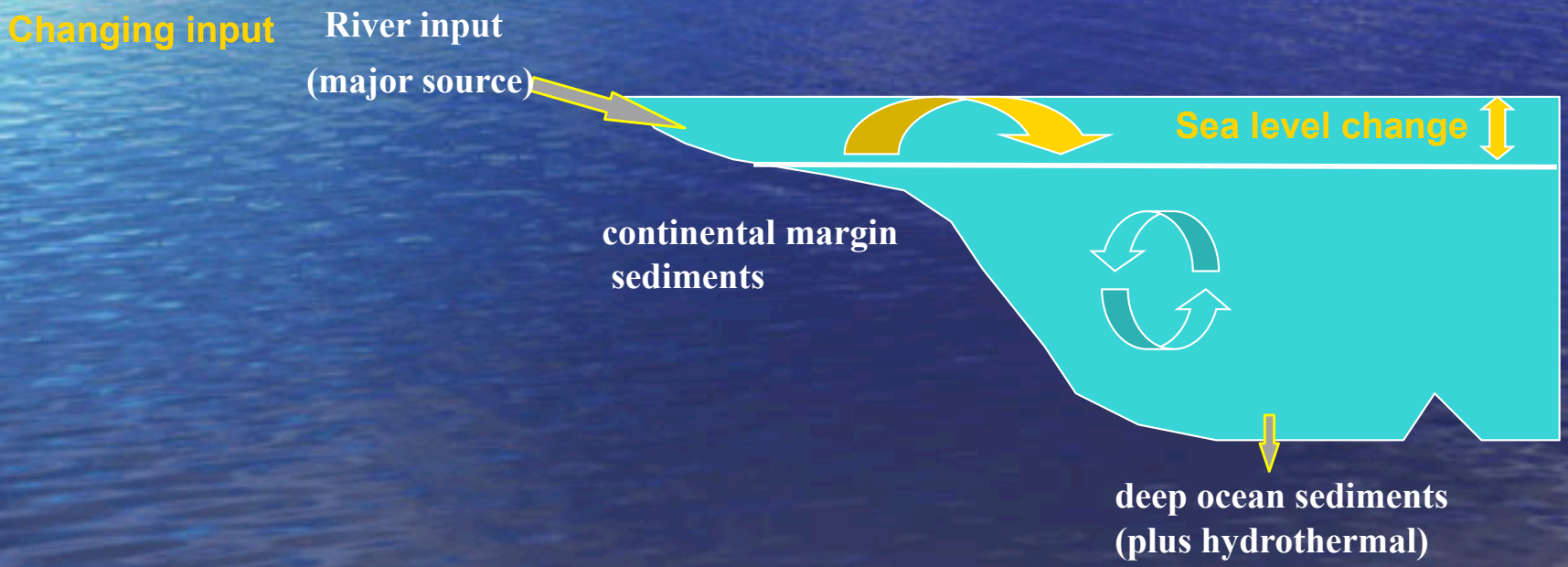
What do we know about internal changes in the mass balance?

Role of continental margins

- Margin sink important in terms of mass balance
- Marginal sedimentation of P very efficient compared to deep sea
- Exposed shelf sediments very susceptible to high release rates of P
- Even internal drivers of the phosphorus cycle may modulate paleoproductivity and thus affect the burial of organic carbon on glacial timescales.

Conceptual model

- Sea-level variations drive phosphorus shelf-deep basin fractionation



CFA—subaerial weathering

What happens when CFA is exposed to subaerial weathering?

Released via congruent weathering reaction

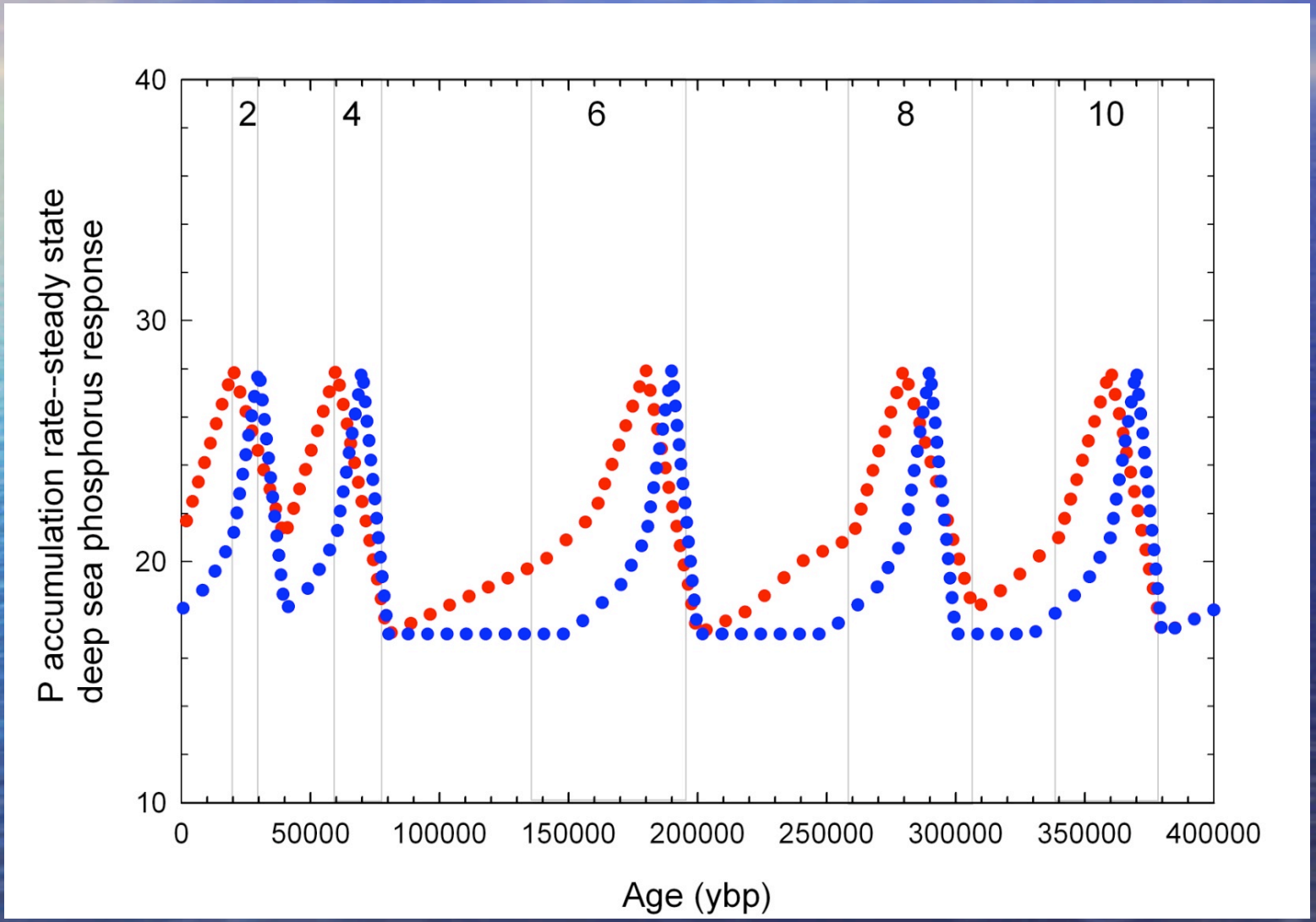
$Ca_5(PO_4)_3OH + 4H_2CO_3 \rightarrow 5Ca^{2+} + 3HPO_4^{2-} + 4HCO_3^{1-} + H_2O$

H_2CO_3—both rainwater and elevated pCO_2 from root respiration

Release also facilitated by phosphatase enzyme and mycorrhizal fungi

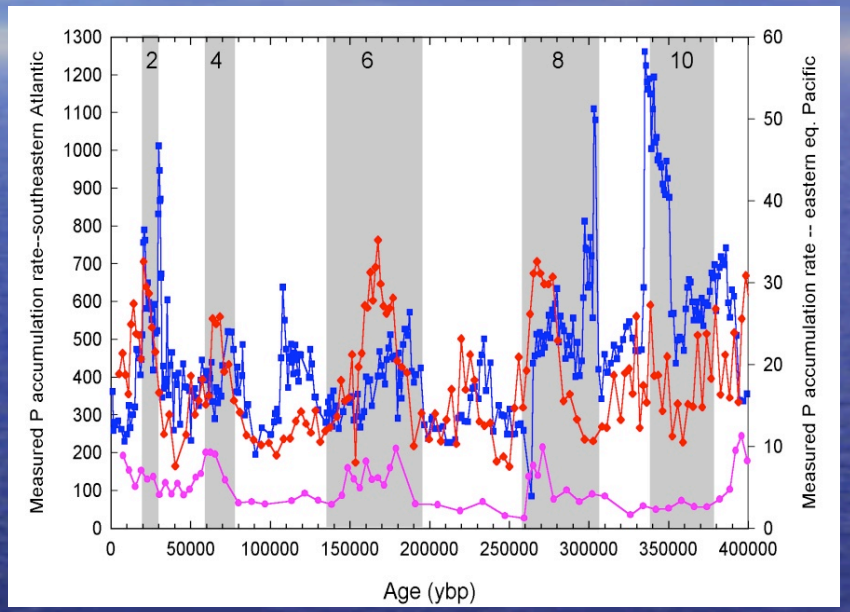
CFA is unreactive in marine sediments but easily dissolved under subaerial weathering (whereas other forms more stable), especially considering high land plant demand

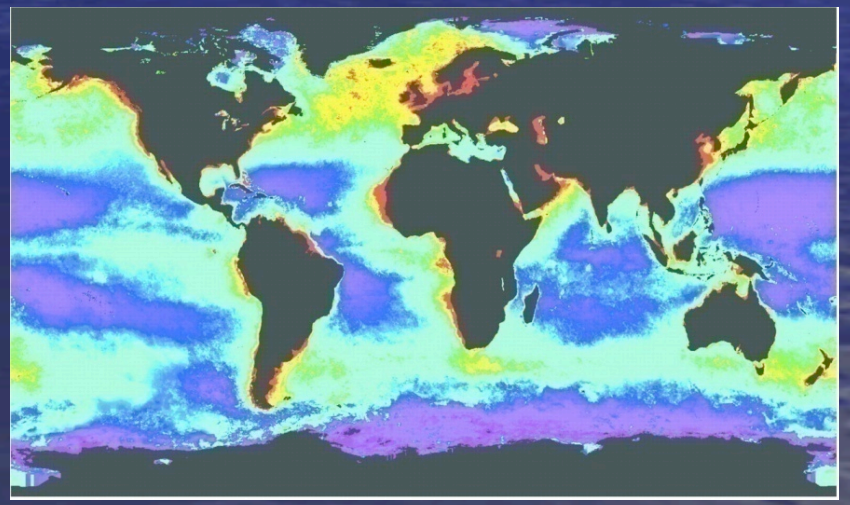
Conceptual model



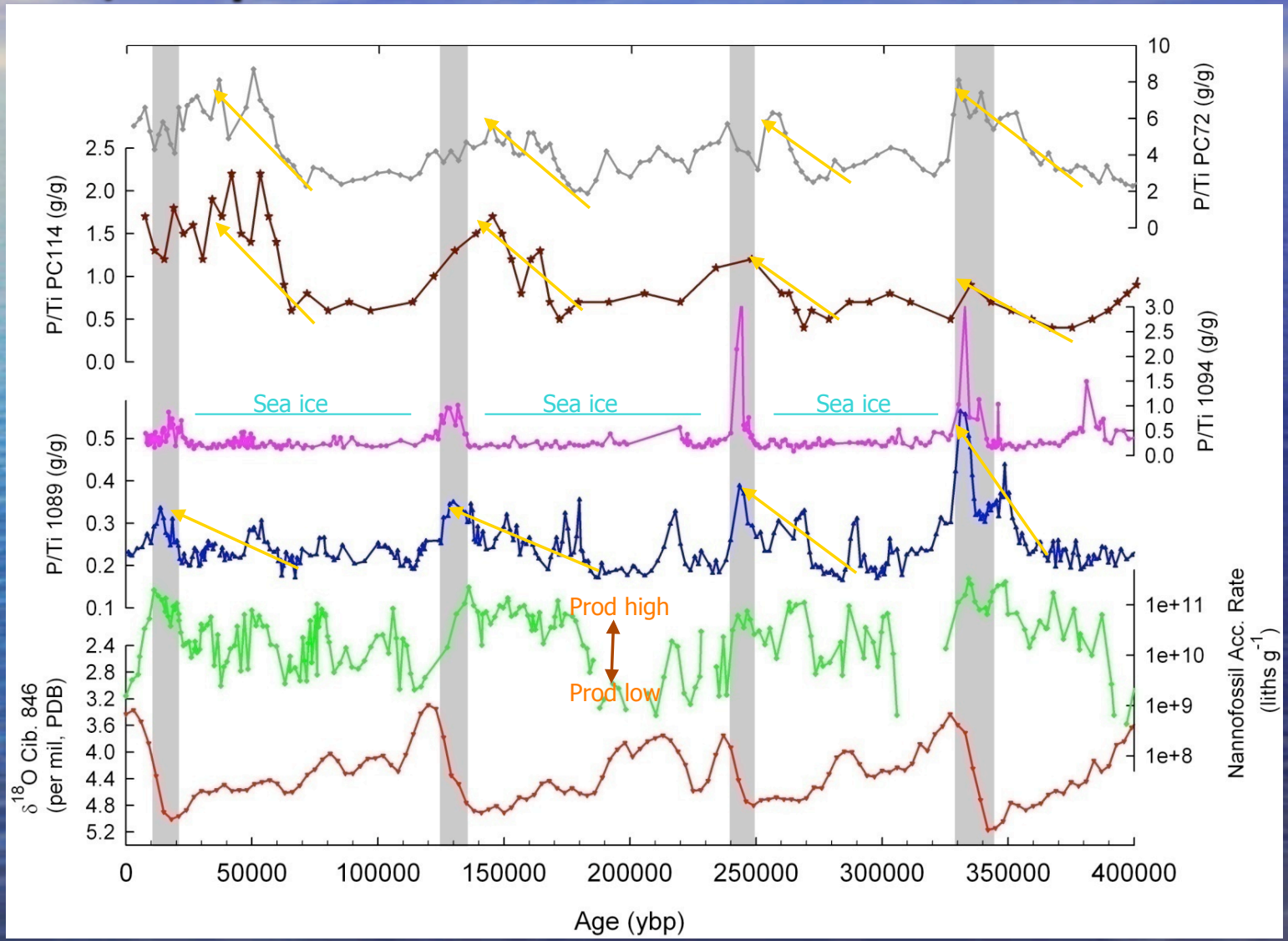
Records of marine phosphorus mass balance variations

- Still do P accumulation rates, but increasingly have been using terrigenously-normalized values (e.g., P/Ti, P/Al) for biologically-related P burial export
  - speed of determination
  - Sedimentation rate models don't apply
  - Can remove some of the sediment focusing influence
- Concentrating on upwelling zones
  - Higher temporal resolution
  - Biological productivity likely most modulated by nutrient supply
  - Export of P highest in these regions, thus most important in terms of marine P mass balance

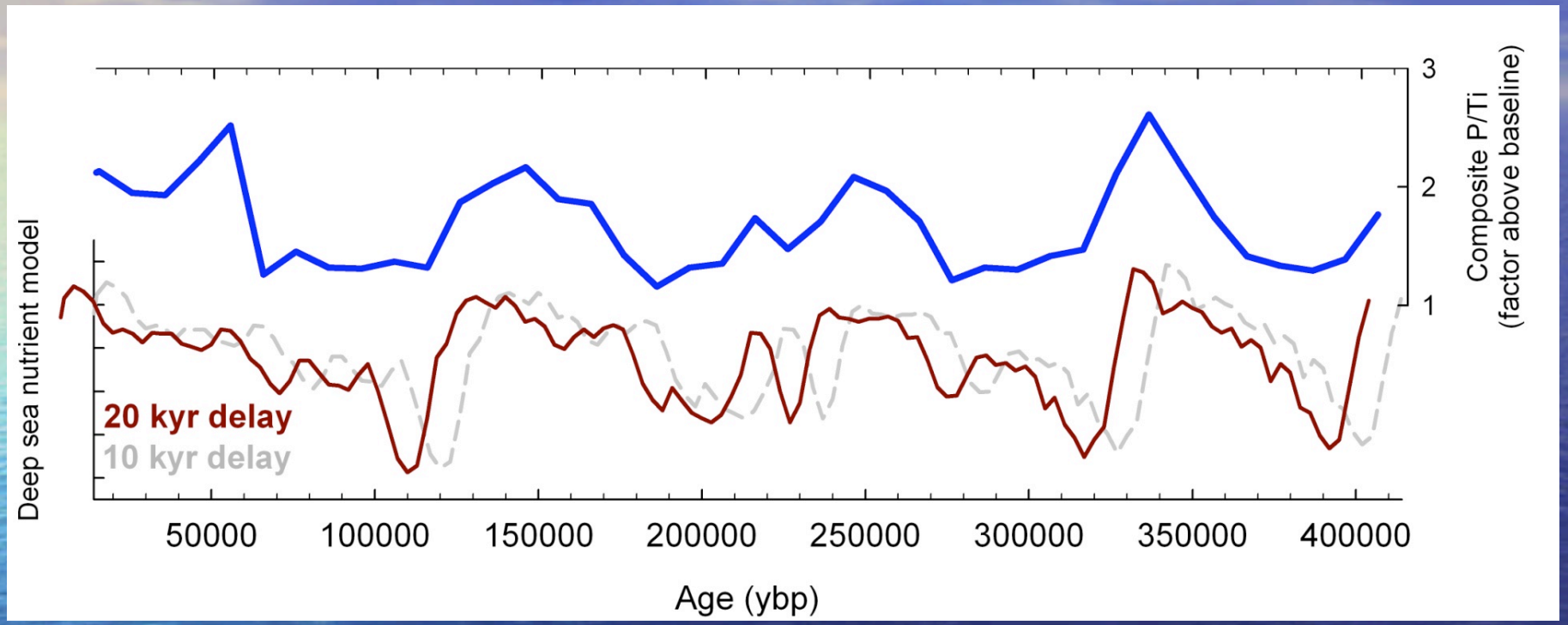




Productivity records from the Southern Ocean, equatorial Pacific



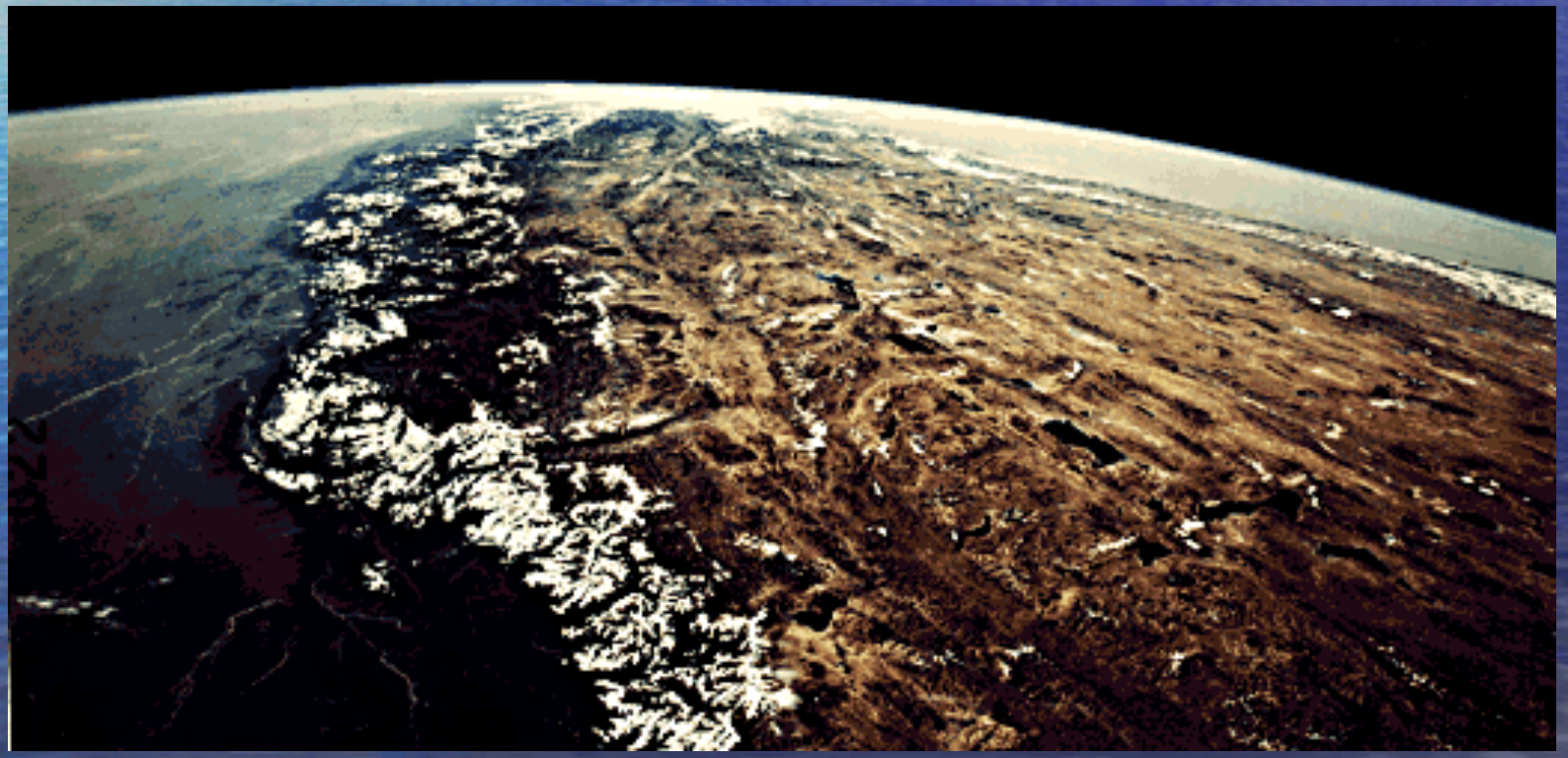
Measured versus Modeled?



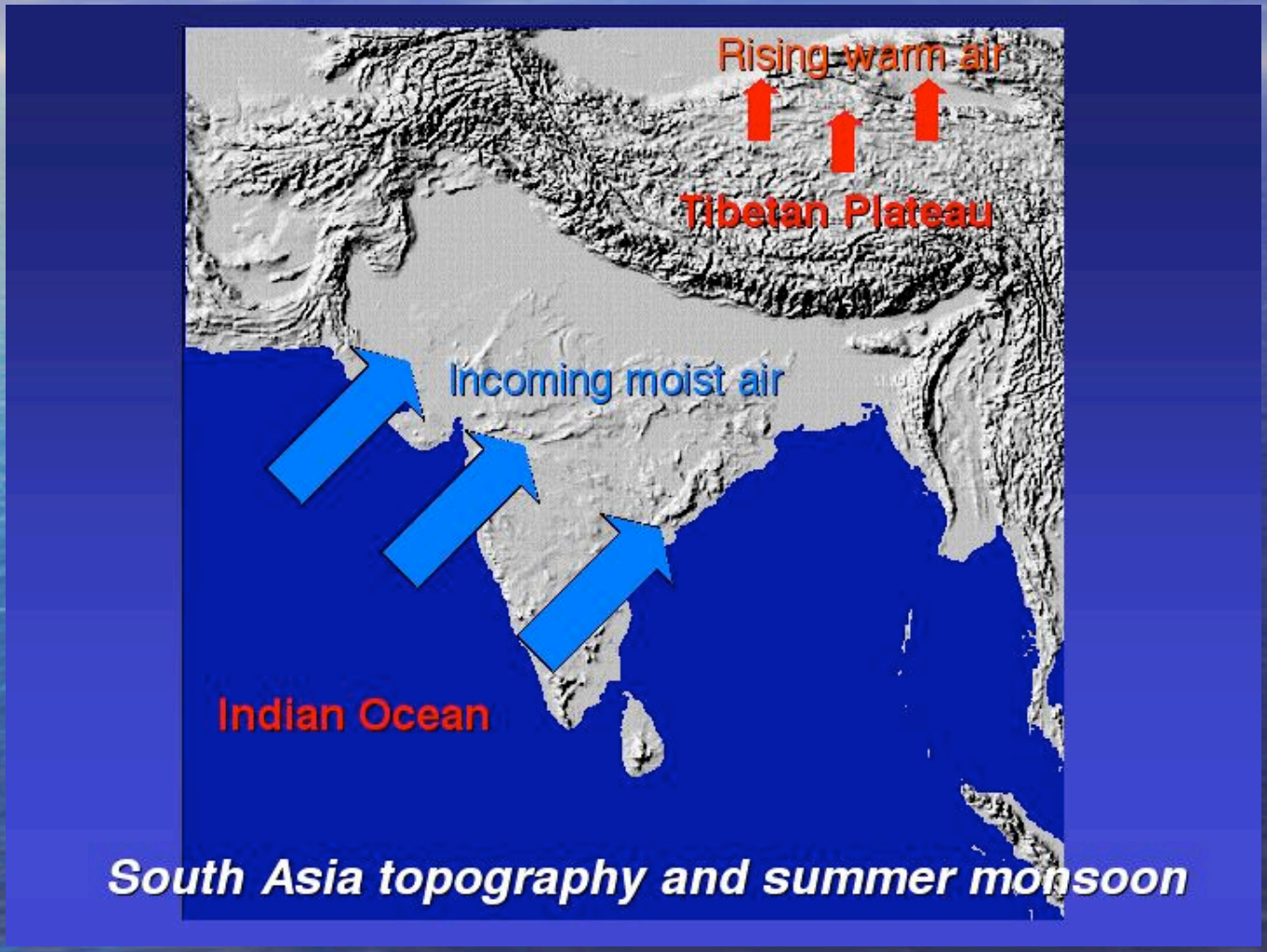
- Model shelf-basin fractionation as a function of sea level
- First-order estimate, more realism than on-off of G/IG but oversimplification
- Why not a more sophisticated model?
  - Assumptions are large
  - Soil processes, weathering, erosion on exposed shelves very difficult to model
  - Input variations from terrestrial system too poorly constrained to make a realistic coupled model

Longer-term variations

- Cenozoic-scale changes related to tectonics
- Himalayan-Tibetan Plateau



Tibetan Plateau and Asian Monsoon



South Asia topography and summer monsoon

Himalayan Uplift
(Raymo, Ruddiman, Froelich)

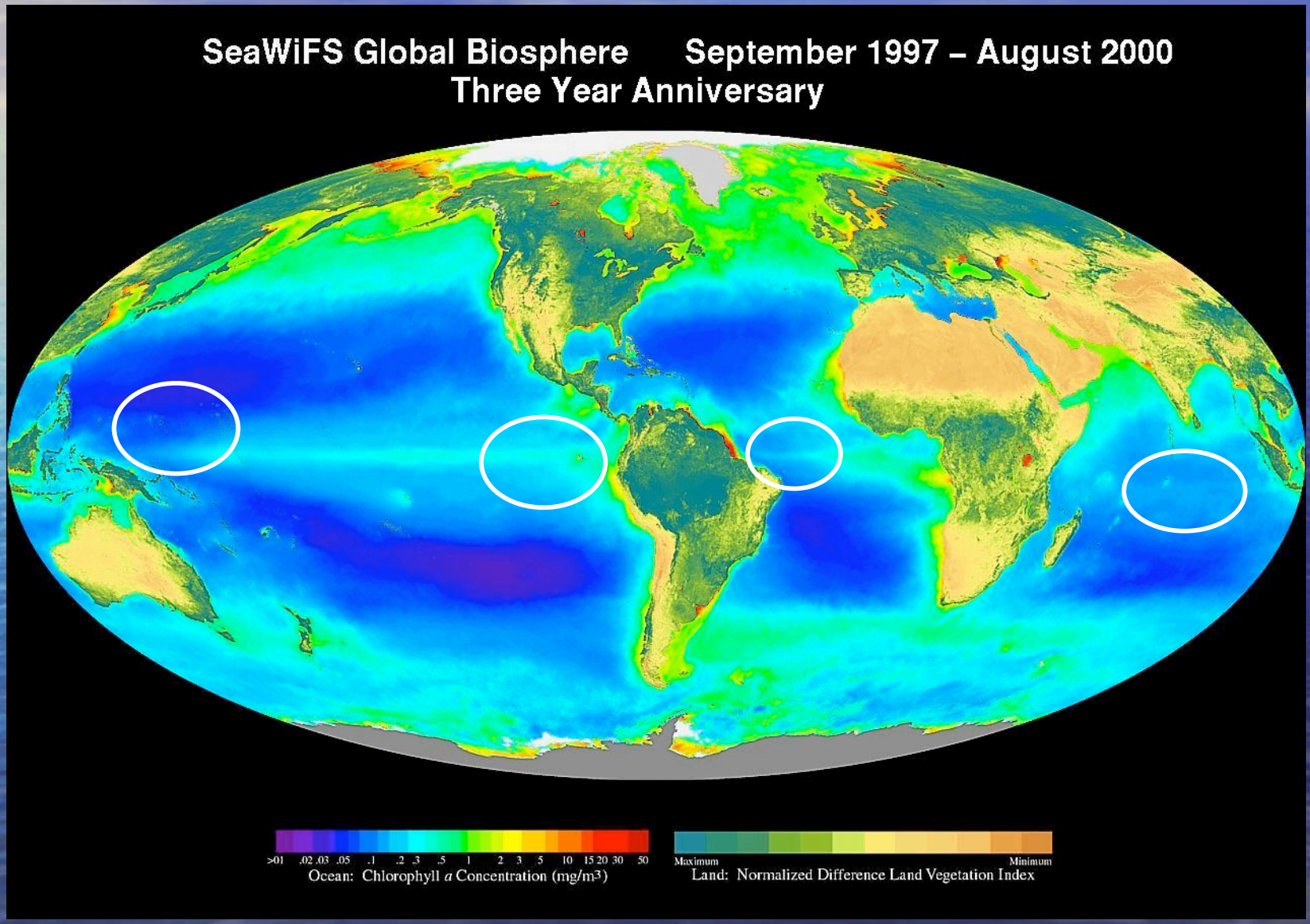
- Problems:

  Does not match well with carbon isotopic records of oceanic productivity, nor Os isotopic records of weathering, nor Ca mass balance record from CCD—Not all weathering is the same

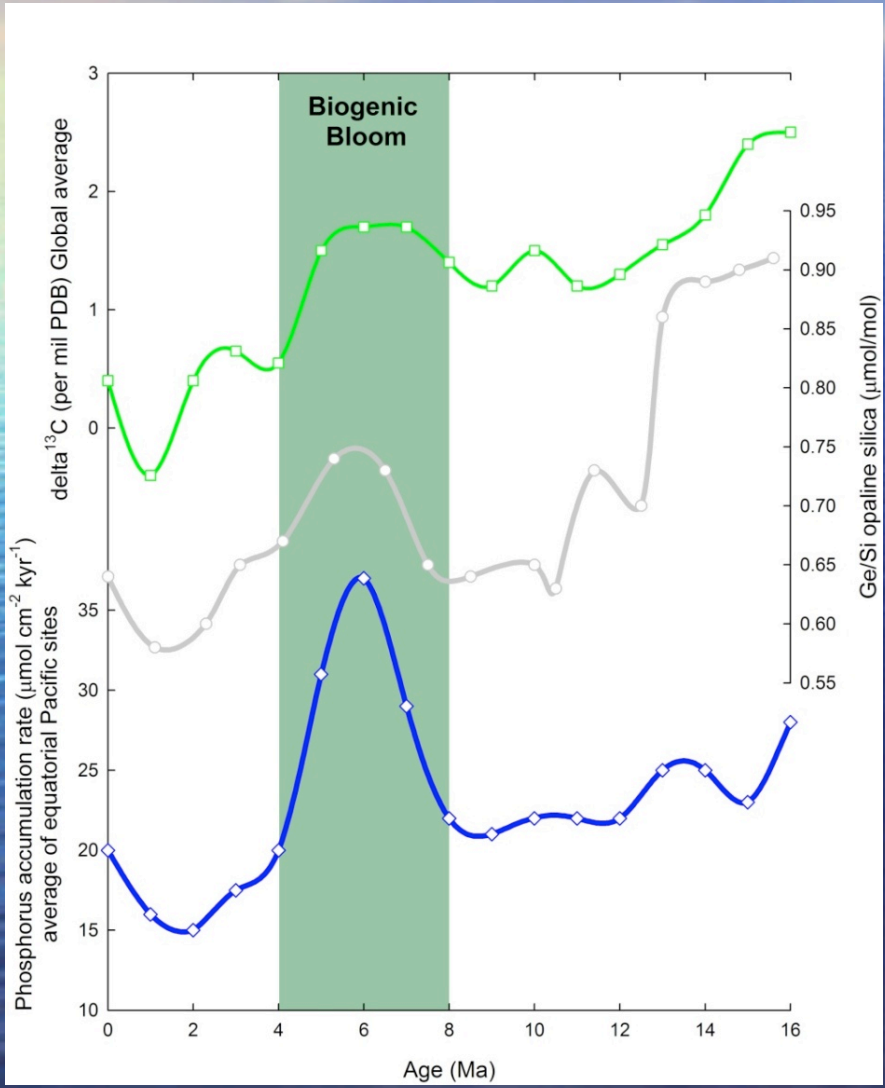
  Examination of Himalayan core complex yields extremely high Sr isotopic composition—could in part be driving radiogenic Sr values

Another Approach: Examine oceanic biogeochemical proxies on shorter time scales, particularly centered around productivity events seen in equatorial records

Records of Phosphorus accumulation



Biogenic Bloom driven by the weathering machine that is HTP



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