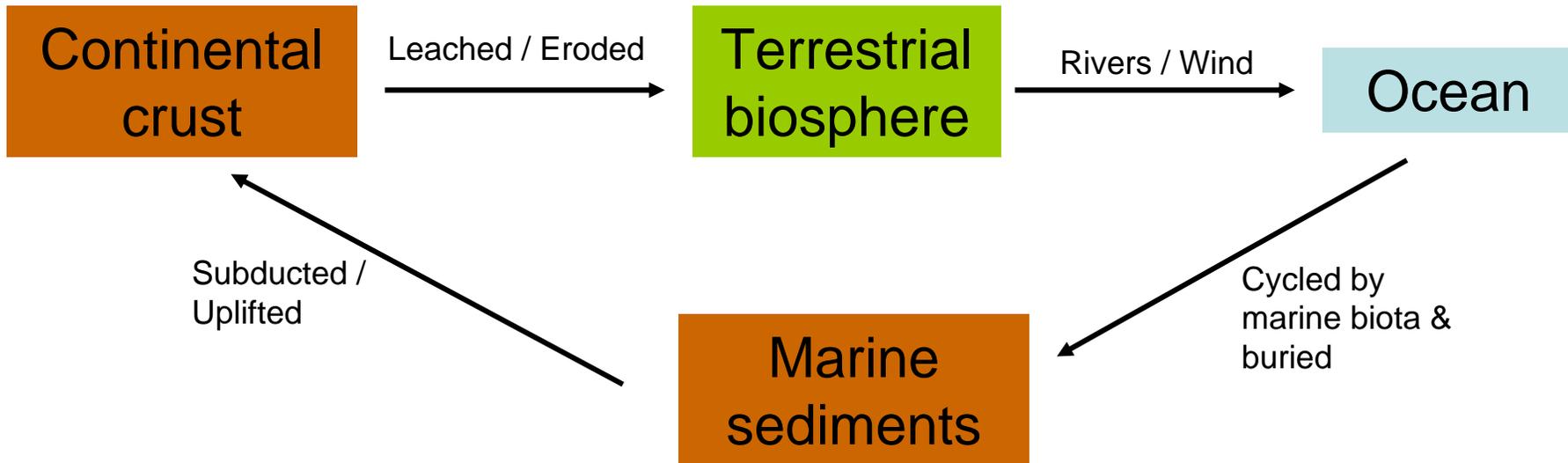
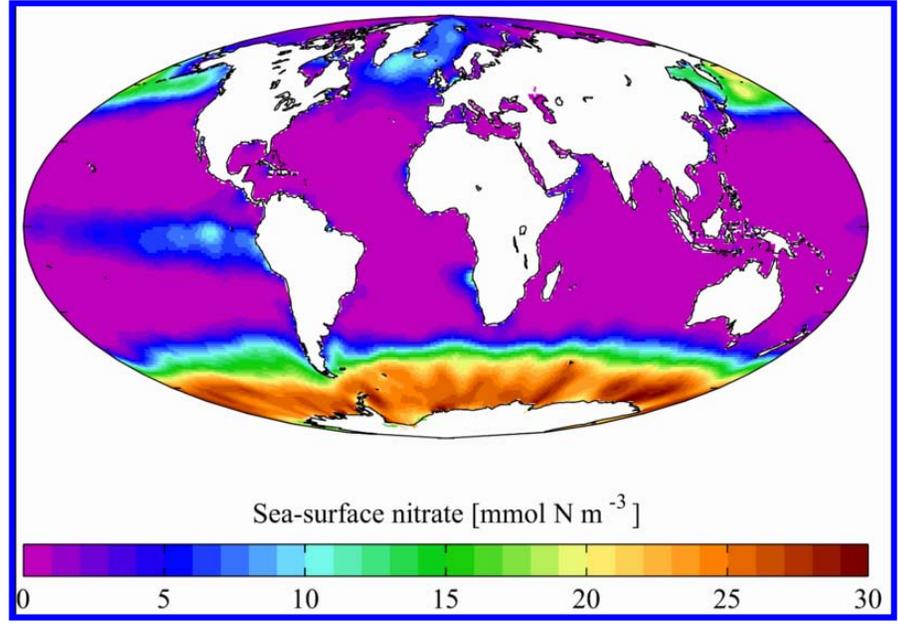
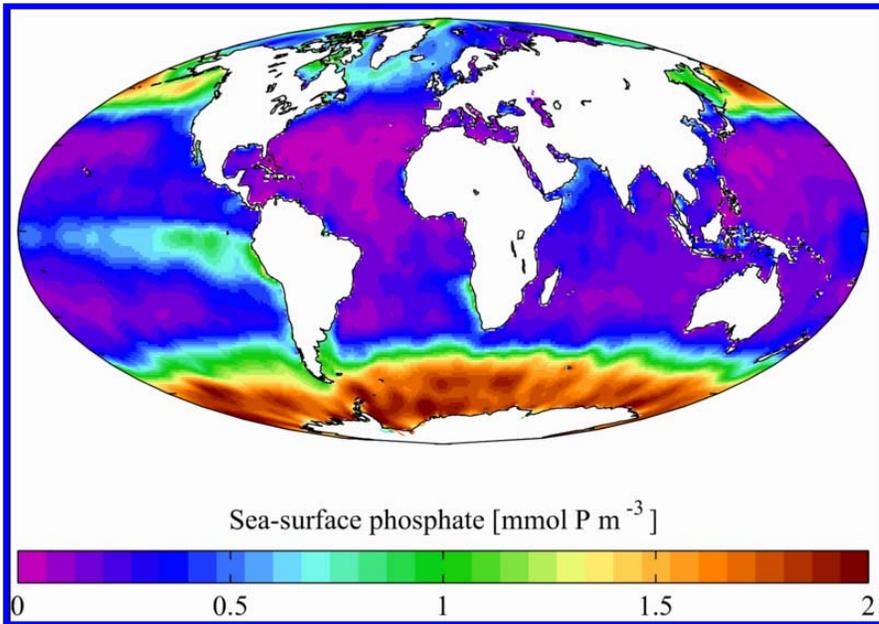


The Global Phosphorus Cycle



- P biogeochemical cycling in the different reservoirs
- Inventories & interactions with other biogeochemical cycles

Why phosphate?



World Ocean Atlas, 2001

- Limiting nutrient on geologic timescales (Tyrell, 1999)
- Need to constrain P budget
- Understand the factors that influence its oceanic inventory

Why phosphate?

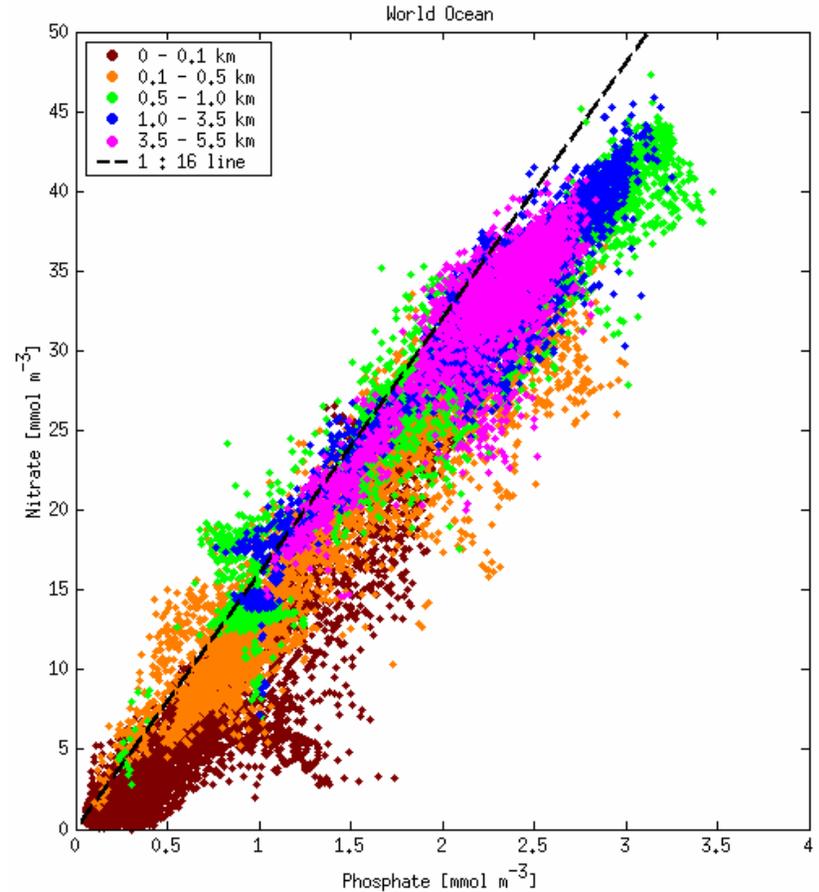
Are oceanic phytoplankton P or N limited?

‘Geochemists’ viewpoint’ :

nitrogen can be "topped up" from the atmosphere by N_2 fixation; phosphorus has no comparable sources or biological pathways

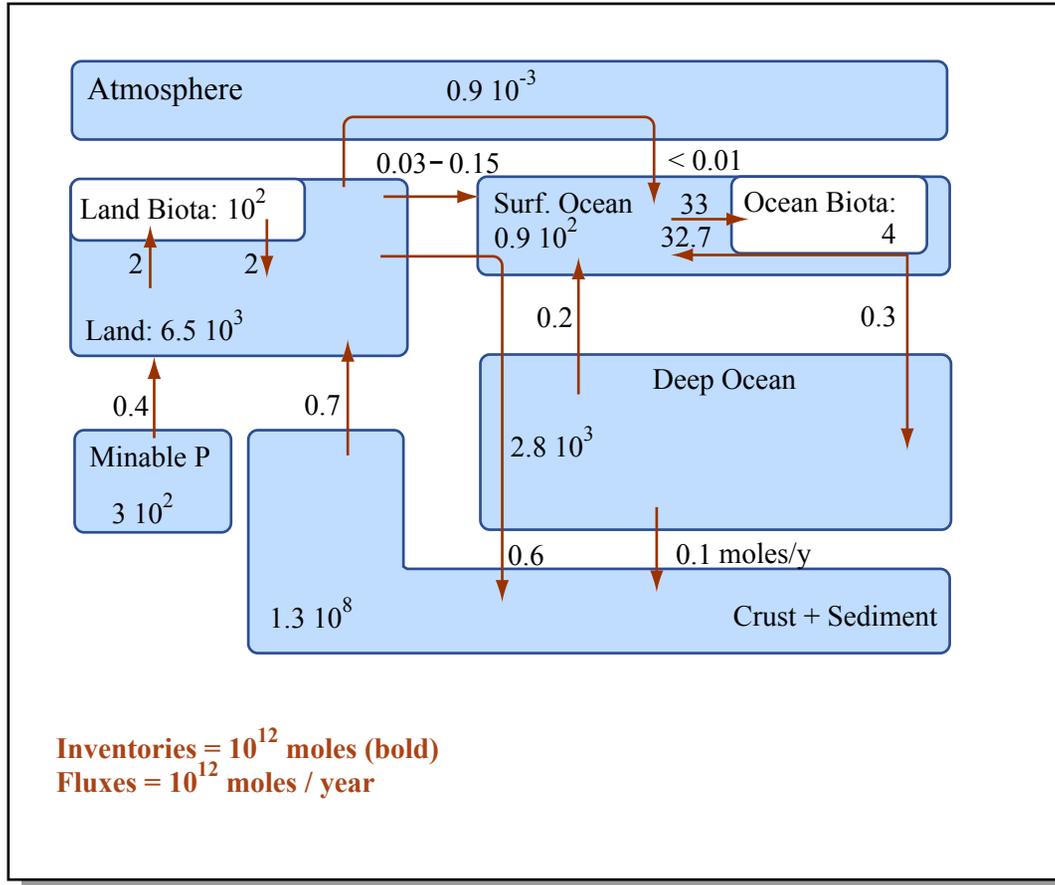
‘Biologists’ viewpoint’ :

observational and experimental work finds natural assemblages of phytoplankton are more N-stressed than P-stressed



Levitus Climatology

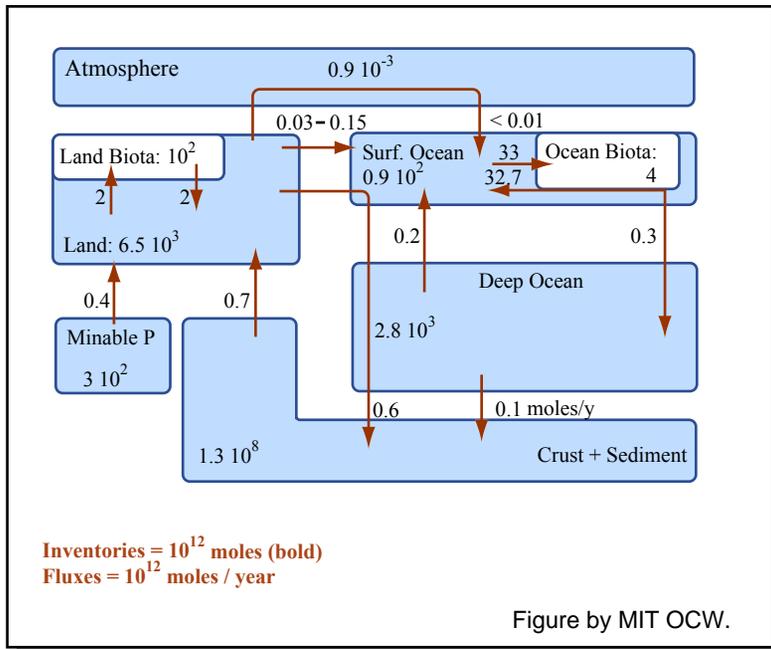
P reservoirs



- Atmosphere not a significant reservoir
- P only occurs in 1 oxidation state (+5), orthophosphate PO_4^{3-}

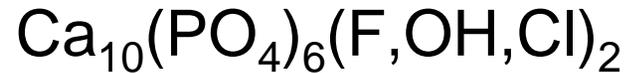
Figure by MIT OCW.

P in the lithosphere



- Largest reservoir

- >95% crustal P = Apatites

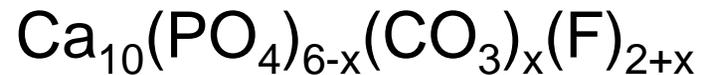


F = fluorapatite

OH = hydroxyapatite

Cl = chlorapatite

- Most common apatite mineral = carbonate fluorapatite



Carbonate partially substitutes for phosphate (PO_4^{3-} vs. CO_3^{2-})

- Not only in igneous rocks...



Apatite minerals

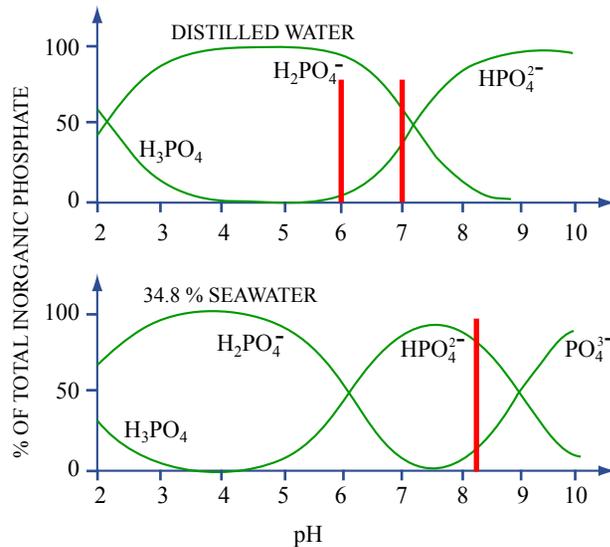
- Hydroxyapatite \Rightarrow produced by biota
- Sedimentary deposits \Rightarrow phosphorite (18-40% P by weight) = fertilizer
- Fluorapatite used in fluoridated water and toothpastes



Anthropogenic processes may change the distribution of the P inventories

P on land & in the biota

- Weathering and erosion of uplifted rocks produce **dissolved** (reactive) and **particulate** (inert) forms of phosphate
- Dissolved P entirely tetrahedral phosphate ions



Distribution of phosphoric acid species as a function of pH in distilled water and seawater. (Atlas, 1975).

Acid / base equilibria

Freshwater pH ~6 – 7 \Rightarrow H₂PO₄⁻

Ocean pH ~ 8.2 \Rightarrow HPO₄²⁻

P on land & in the biota

- ***Dissolved*** (reactive) is taken up & cycled by terrestrial biota
- Produces organophosphates (P_{org}), phosphate esters

Most important P-containing organic molecules are DNA, RNA, ATP, & phospholipids

Phospholipids \Rightarrow phosphate esters produced with fatty acids containing hydrophobic C chains (important constituent of cell membranes)

Chemical Structure of RNA, DNA, and ATP.
Image removed due to copyright restrictions.

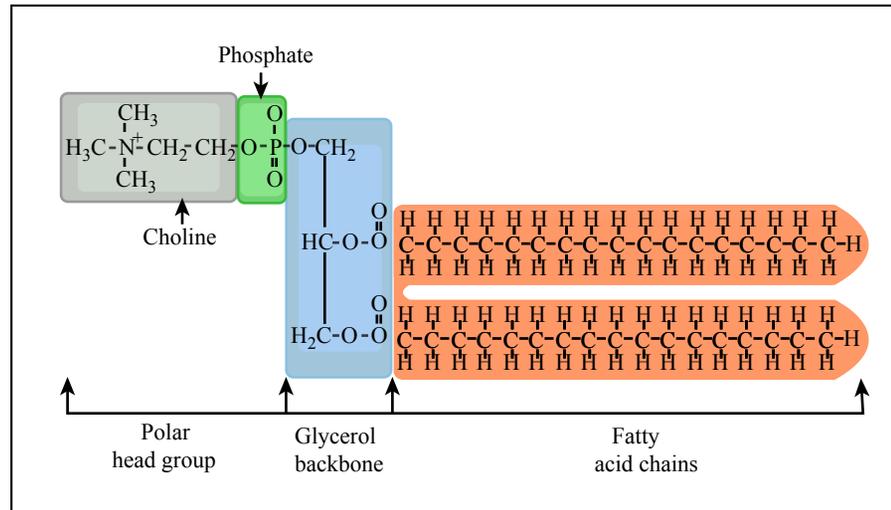


Figure by MIT OCW.

P on land & in the biota

- Dissolved phosphate concentrations are low in soil:
Adsorbed onto clays, Fe and Al oxides
- Terrestrial systems are often ***P limited***
Plants ↑ P availability via chelating compounds
- C / P (moles / moles) marine organisms ~ 106 (Redfield)
- C / P terrestrial plants >> 106
- Terrestrial plants contains less P per mole C due to:
Higher proportion of structural C-rich and P-poor molecules, carbohydrates and lignins

P on land & in the biota

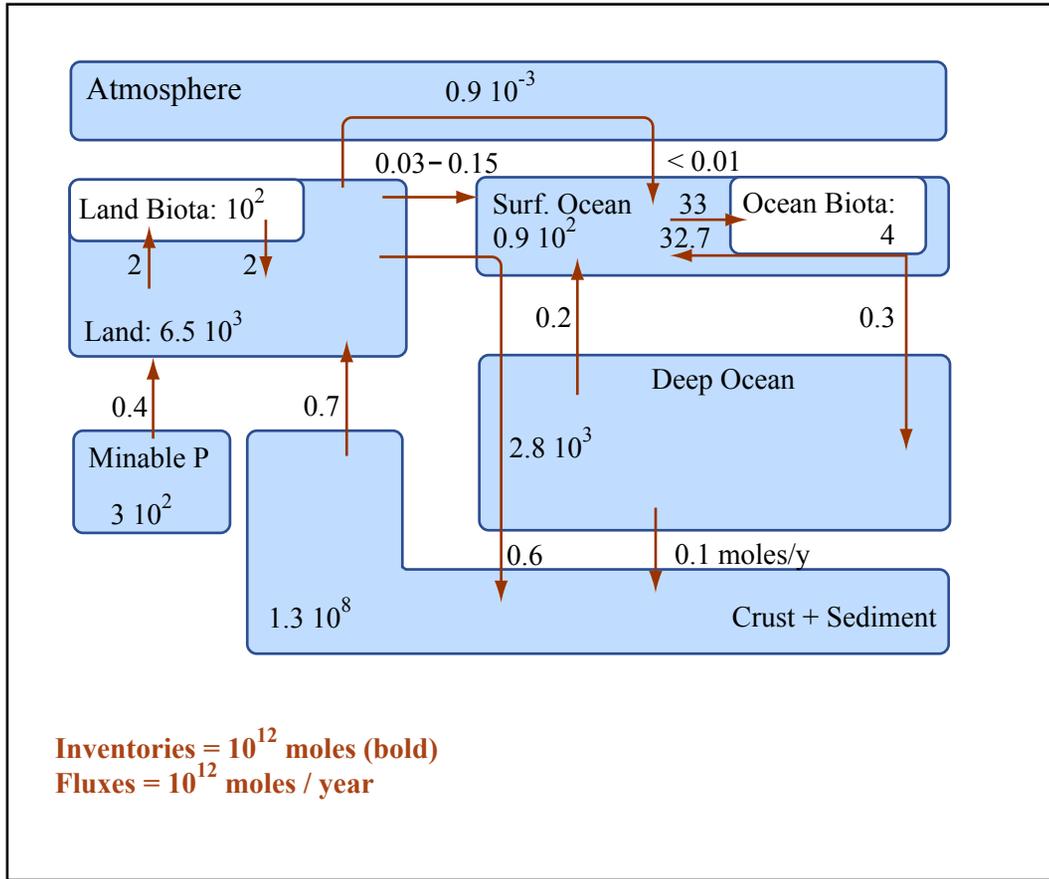


Figure by MIT OCW.

Turnover time of land biota:

$$10^{14} \text{ moles} / 2 \times 10^{12} \text{ moles yr}^{-1}$$

~ 50 years

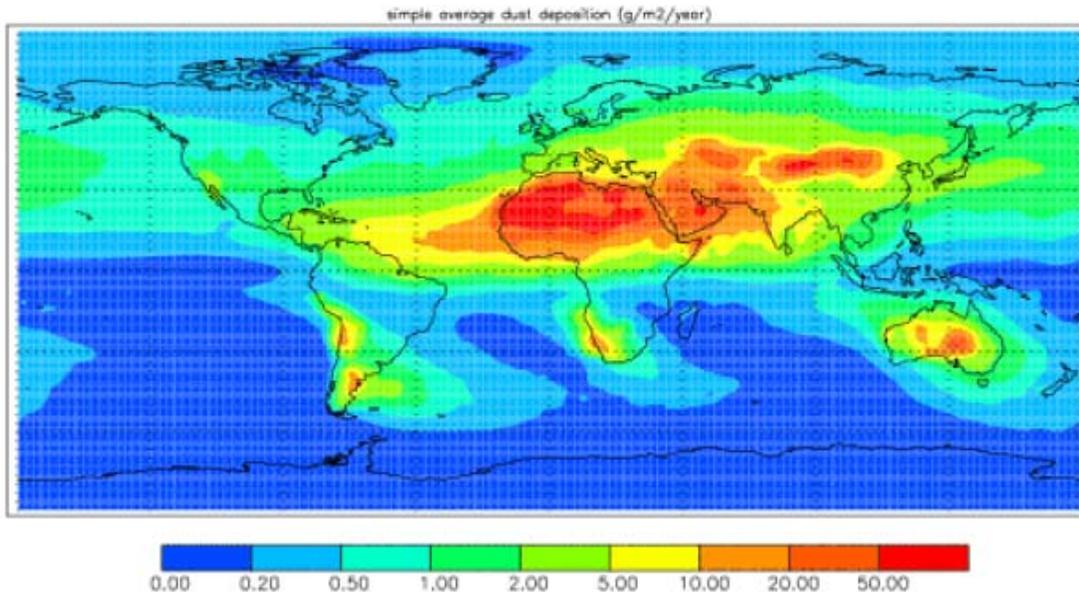
Retention time of reactive & eroded P on land:

$$6.5 \times 10^{15} \text{ moles} / 0.7 \times 10^{12} \text{ moles yr}^{-1}$$

~ 9000 years

P transport to the ocean - Aeolian

- Small source due to Aeolian transport of dust (no gaseous forms of P)



Mahowald et al., 2005a

Dust input to the ocean is highly variable: spatially, seasonally (rainfall & transport patterns), glacial-interglacial, episodic (wind speed)

Total dust flux

x

Mean [P] in aerosols

x

solubility

= Total Aeolian P flux

P transport to the ocean - Aeolian

$$\text{Total dust flux} \times \text{Mean [P] in aerosols} \times \text{solubility} \\ = \text{Total Aeolian P flux}$$

Solubility of dust P \Rightarrow 21 – 51% (Graham and Duce, 1982)

Aeolian input of reactive P \Rightarrow 0.01 – 0.02 x 10¹² moles yr⁻¹

Aeolian input \lll fluvial input

Even in oligotrophic gyres:

estimates of Aeolian input account
for less than 1% of new production

Aeolian input of P (10 ⁹ g/year)	
North Pacific	500
South Pacific	41
North Atlantic	230
South Atlantic	25
North Indian	110
South Indian	46
Global Total	950

Factor of 2-3 uncertainty

P transport to the ocean - Fluvial

- Rivers are the primary source of P for the oceans
- 90-95% of P in river is in particles:
 - Inert minerals directly eroded from continental crust
 - Fe and Al oxides (P adsorbed as oxides & clay)
- In estuaries reactive P can be:
 - Desorbed from Fe oxides and clays
 - Removed into estuarine sediments as P_{org} after biological uptake, by salinity induced flocculation of Fe-humic river colloids
- Small amounts of P desorption can greatly $\uparrow\uparrow$ our estimates of the fluvial input of bioavailable phosphate
- Current estimates $0.03 - 0.15 \times 10^{12}$ moles yr^{-1}

P cycling in seawater

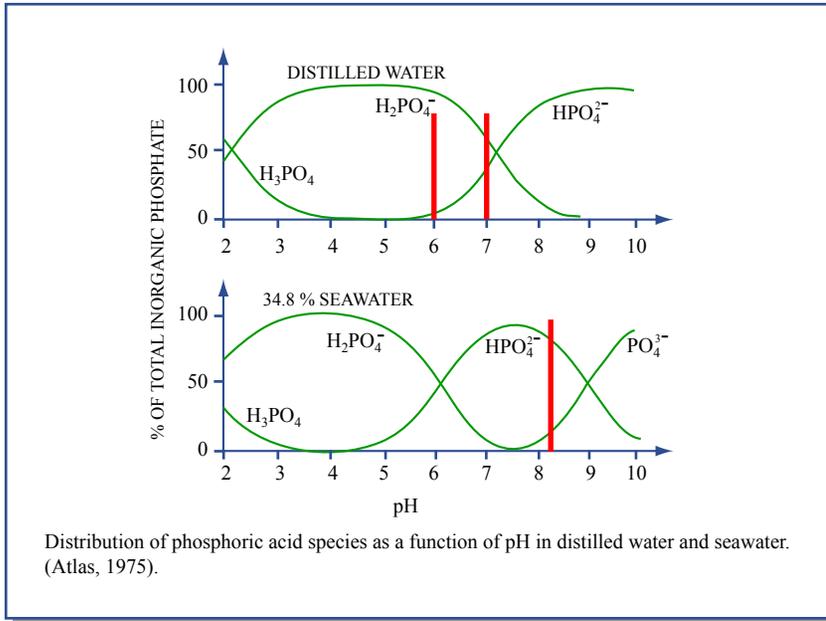


Figure by MIT OCW.

In seawater dissolved inorganic phosphorus primarily HPO_4^{2-}

Ion pairs are formed with the major cations in seawater

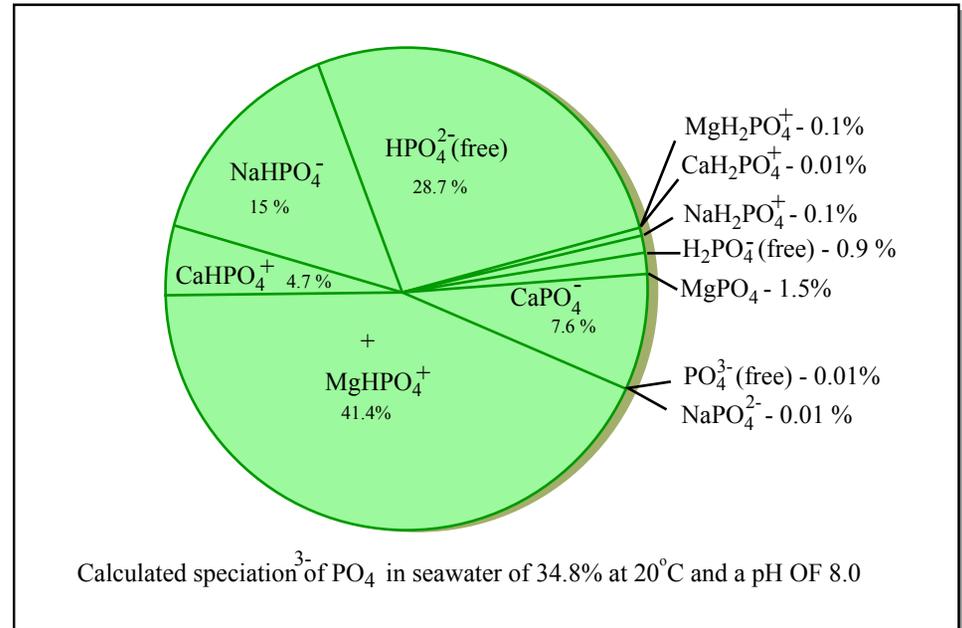


Figure by MIT OCW.

P cycling in seawater

Dissolved P fractions in are operationally defined:

Soluble Reactive Phosphorus (SRP) is measured in filtered seawater as the fraction of phosphate that can be measured directly by the colorimetric phosphomolybdate method. This fraction is believed to consist mainly of inorganic phosphate, but may also encompass some acid-labile organic compounds.

Total Dissolved Phosphate (TDP) is measured by the phosphomolybdate method in filtered seawater, after treatment with a strong oxidizing reagent.

Soluble Non-Reactive Phosphate (SNP) is calculated by difference ($SNP = TDP - SRP$) and is thought to consist mainly of dissolved organic phosphate (DOP) and polyphosphates.

P cycling in seawater

SNP (or DOP) is a large % of total dissolved P in surface oligotrophic waters (Wu et al., 2000)

Is biolimiting so most of it is within phytoplankton cells

DOP is converted back to inorganic P via enzymatic and microbial remineralization processes

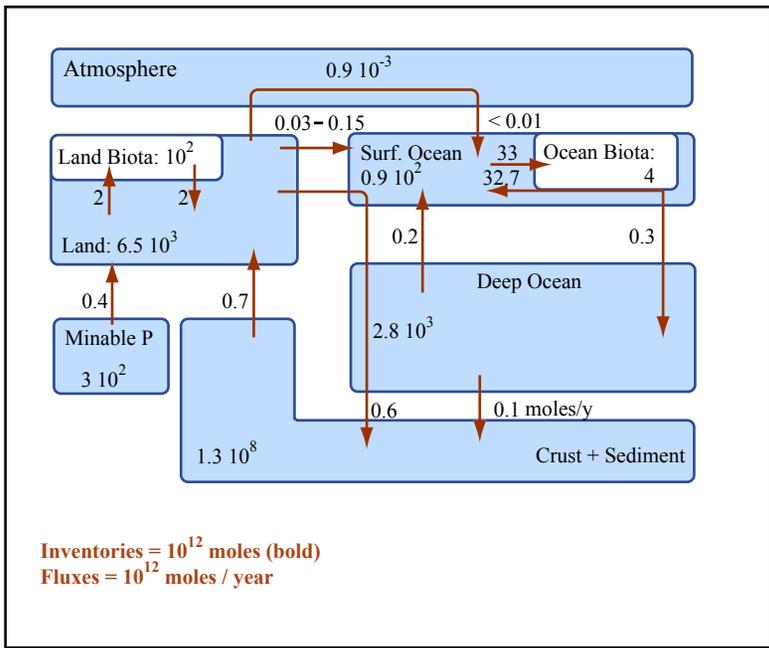


Figure by MIT OCW.

Oceanic biota reservoir smaller than land reservoir BUT the fluxes between reactive P & the biota are much larger

4×10^{12} moles / 33×10^{12} moles yr⁻¹
~ 0.12 years

Dominance of single celled organisms with short lifetimes

P cycling in seawater – field methods

- Can be studied using 2 natural radioactive P isotopes:

^{32}P (14.3 dys) and ^{33}P (25.3 dys), cosmogenic isotopes from Argon

Rapidly removed onto aerosols, added to seawater via rain

- $^{33}\text{P}/^{32}\text{P}$ in rainwater varies little but $^{33}\text{P}/^{32}\text{P} \uparrow\uparrow$ with time

$$[^{33}\text{P}/^{32}\text{P}]_0 e^{(\lambda_{33} - \lambda_{32})t}$$

- High $^{33}\text{P}/^{32}\text{P}$ = an older P pool

P cycling in seawater – field methods

- Measure P isotopic ratio in different pools (inorganic P, DOP, phytoplankton, zooplankton, etc.)

Estimate age

Turnover of P within the pools

Pathways of P through the food chain

- Need to constrain the $^{33}\text{P} / ^{32}\text{P}$ of rain water
- Preliminary studies \Rightarrow DOP turnover rates vary widely in space and time

P cycling in seawater – turnover time

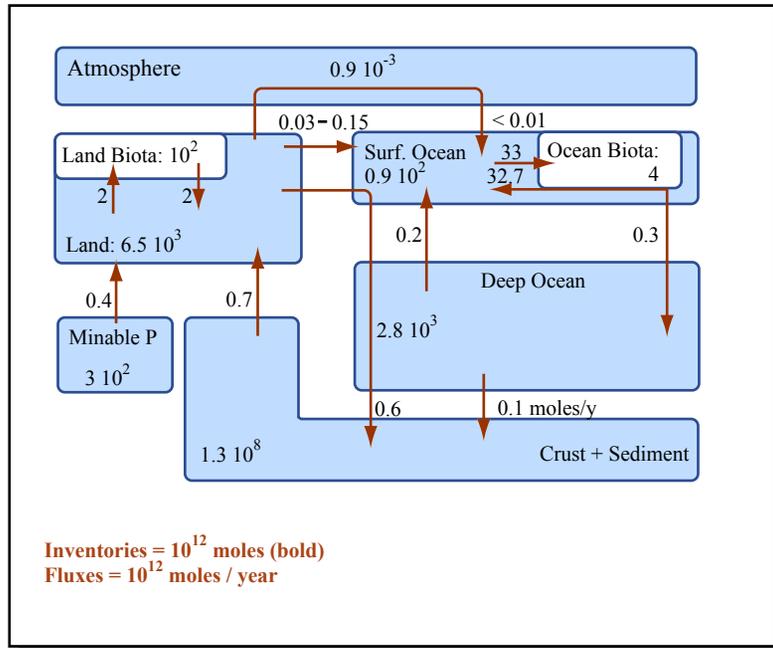


Figure by MIT OCW.

Surface seawater P turnover:
 90×10^{12} moles / 33×10^{12}
 moles yr^{-1}
 ~ 2.7 years

Small fraction is exported (but
 very few direct measurements)

Mean residence time in surface
 waters of 9 years

Rate of P_{org} export: C export dataset * $\text{mean}(P/C)_{\text{org}}$

Global export production $\sim 10^{15}$ moles C yr^{-1} (Laws et al., 2000)

Average $C/P_{\text{org}} = 117 \pm 14 \Rightarrow 10^{13}$ moles P yr^{-1}

P delivery to the seafloor

- Global C_{org} delivery rate to the seafloor below 1000 m is estimated to be equivalent to an O_2 consumption of 54.4×10^{12} moles yr^{-1} (Janke, 1996)
- Anderson & Sarmiento, 1994 demonstrated that $(-O_2/P)_{\text{org}}$ of particles sinking to the deep sea is 170 ± 10
- P delivery is thus:
 - 54.4×10^{12} moles O_2 yr^{-1} / 170 moles O_2 moles P^{-1}
 - $= 0.32 \times 10^{12}$ moles P $\text{yr}^{-1} \Rightarrow \sim 3\%$ of the export flux
 - $= 97\%$ of the P_{org} is remineralized in the deep sea

How much P is buried

- Degradation of organic P in sediments \Downarrow amount of organic P buried, extensive P recycling due to remineralization
- \Uparrow porewater phosphate concentrations = diffusive flux of P *out* of sediments
- Deep-sea sediment flux measurements extrapolated to the global ocean suggest an efflux of P from the sediments $>$ or $=$ to the rate of P delivery from surface export (Henson et al., 1998)
- Much of the P_{org} & C_{org} delivered to the seafloor is remineralized
- Burial = delivery – efflux, both of which are poorly constrained

How much P is buried

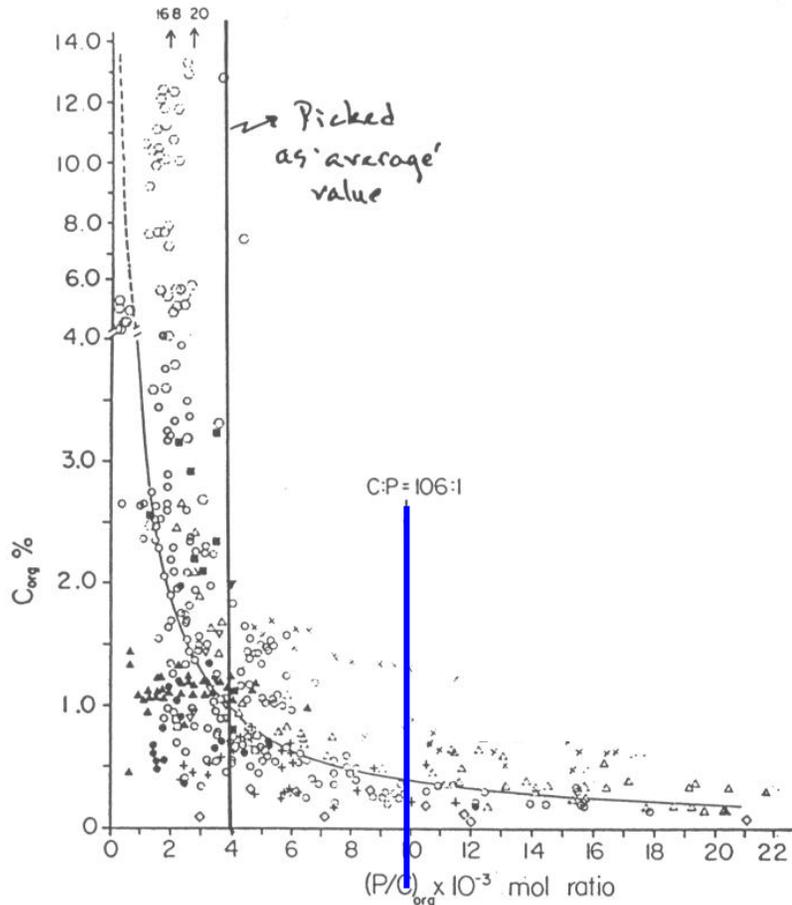
- Rate of organic P burial =

$$C_{\text{org}} \text{ burial rate estimates} * \text{mean buried } (C/P)_{\text{org}}$$

- C_{org} burial rates at depths > 1000 m are $\sim 1.25 \times 10^{12}$ moles yr^{-1} , $< 3\%$ of delivery
- Large amounts are buried at shallower depths (total burial as high as 10×10^{12} moles yr^{-1} (Berner, 1982)
- If we assume Redfield (106 C : 1 P) in sediments deposited at depths > 1000 m
 - \Rightarrow Maximum P_{org} burial rate is 1.25×10^{12} moles $\text{yr}^{-1} / 106 = 1.1 \times 10^{10}$ moles yr^{-1}
- Estimates that take into account shallower sediments range from 4.1 to 18.5×10^{10} moles yr^{-1} (e.g. Ruttenberg, 1993)

How much P is buried

- The effect of organic matter degradation on the C/P of buried organic material has not been demonstrated



C / P of buried organic matter:

- is highly variable
- varies systematically with $\%C_{org}$
- Often $>$ Redfield, preferential release of P over C to bottom water before final burial

Courtesy of Froelich et al. Used with permission.
Froelich, P.N., Bender, M.L., Luedtke, N.A., Heath, G.R. & Devries, T.
"The marine phosphorus cycle." *American Journal of Science* 282
(1982): 474-511.

How much P is buried

- But in contrast a later study suggested systematic changes in the C / P ratio of buried organic material and preservation of organic matter with sedimentation rates (Ingall and van Cappellen, 1990)
- C / P of buried organic matter close to Redfield at high ($> 1 \text{ cm yr}^{-1}$) and low ($< 0.002 \text{ cm yr}^{-1}$) sedimentation rates & higher at intermediate rates

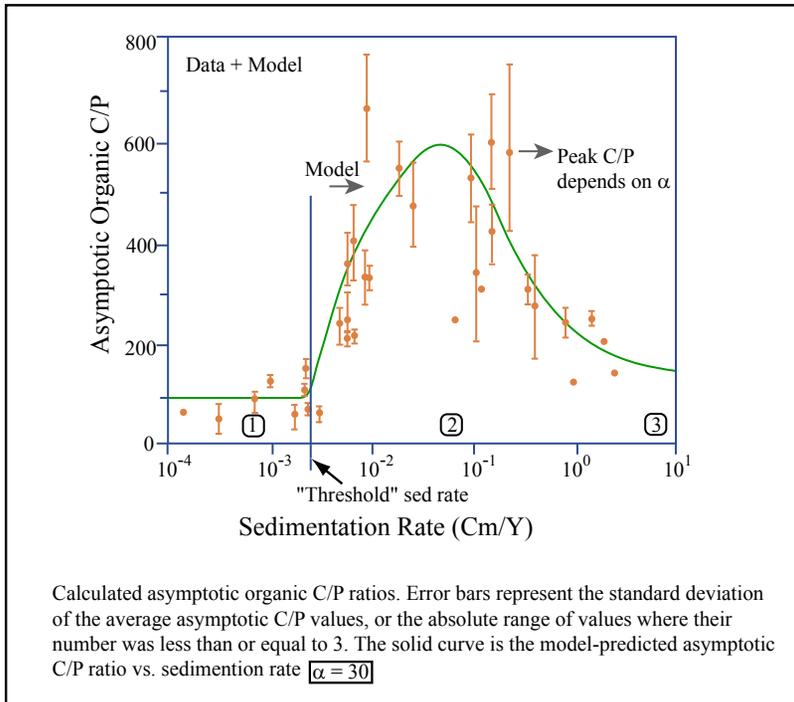
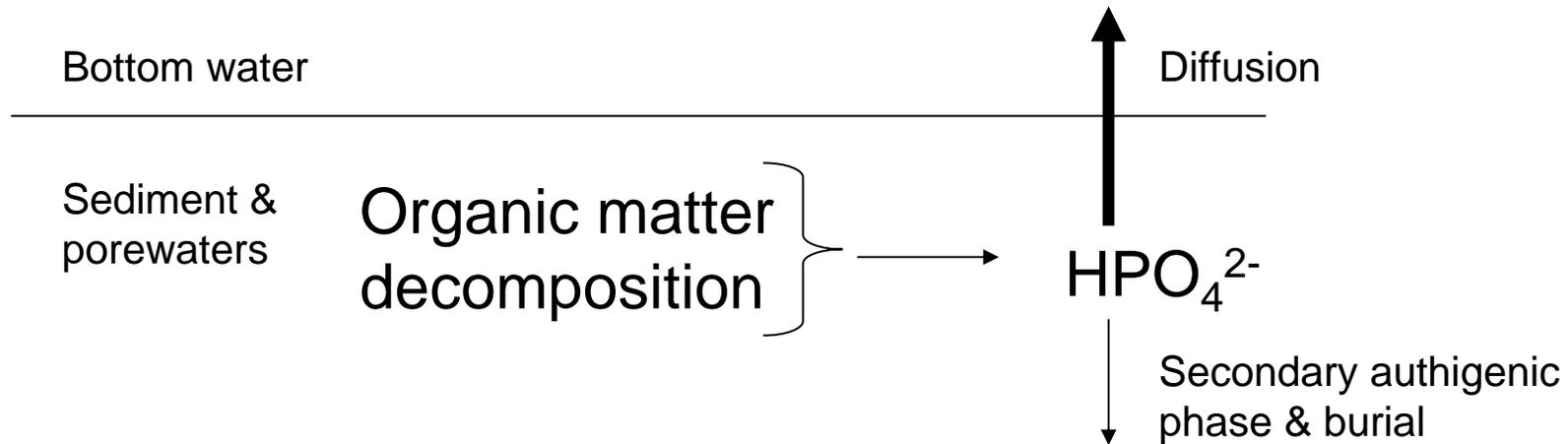


Figure by MIT OCW.

- Oxidic respiration \Rightarrow assume P is remineralized preferentially to C
- Very high sedimentation rates = good preservation of organic material, C/P close to Redfield
- Very slow sedimentation rates, remineralization is nearly complete, producing a low C/P ratio
- Mid range sedimentation rates reflect preferential regeneration of P, higher C / P would \downarrow the importance of margin sediments as a sink for P

Chemical nature of buried P in sediments



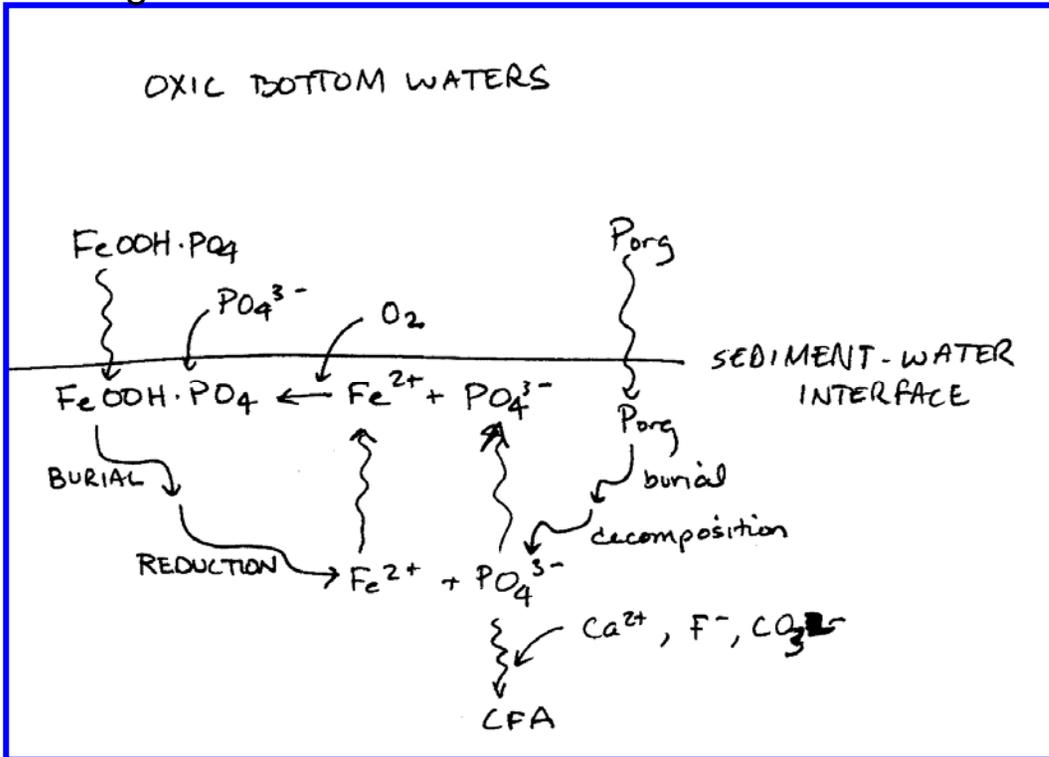
- Fate of the released HPO_4^{2-} in porewaters ultimately dictates the C / P of marine sediment
- P can be buried as:
 - Refractory organic P
 - Carbonate fluorapatites formed in sediments
 - Absorption of dissolved P to Fe oxides in hydrothermal plumes
 - Low temperature basalt interaction at hydrothermal vents

The impact of O_2 on P burial

- The extent of P burial also seems to depend on the presence of O_2 in bottom waters
- In the presence of O_2 preservation of C_{org} ↓ while that of P ↑ (low C / P)
- Due to the presence of Fe oxide layers near the sediment water-interface which trap P released from organic matter decomposition
- If no little or no O_2 is present, more C_{org} is preserved but P released from organic matter remineralization is more likely to diffuse to the overlying water layer (C / P > Redfield)

Chemical nature of buried P in sediments

P diagenesis in sediments



In sediments underlying coastal upwelling and most margin regions CFAs are often observed

CFAs precipitate from porewaters where phosphate concentrations near the sediment-water interface are high as a result of release from Fe oxide dissolution & Fe recycling

As iron oxides are buried and reduced the adsorbed P is released to the pore water, building up phosphate at each cycle

Chemical nature of buried P in sediments

CFA precipitation documented with a leaching procedure that differentiates between the different forms of P in sediments

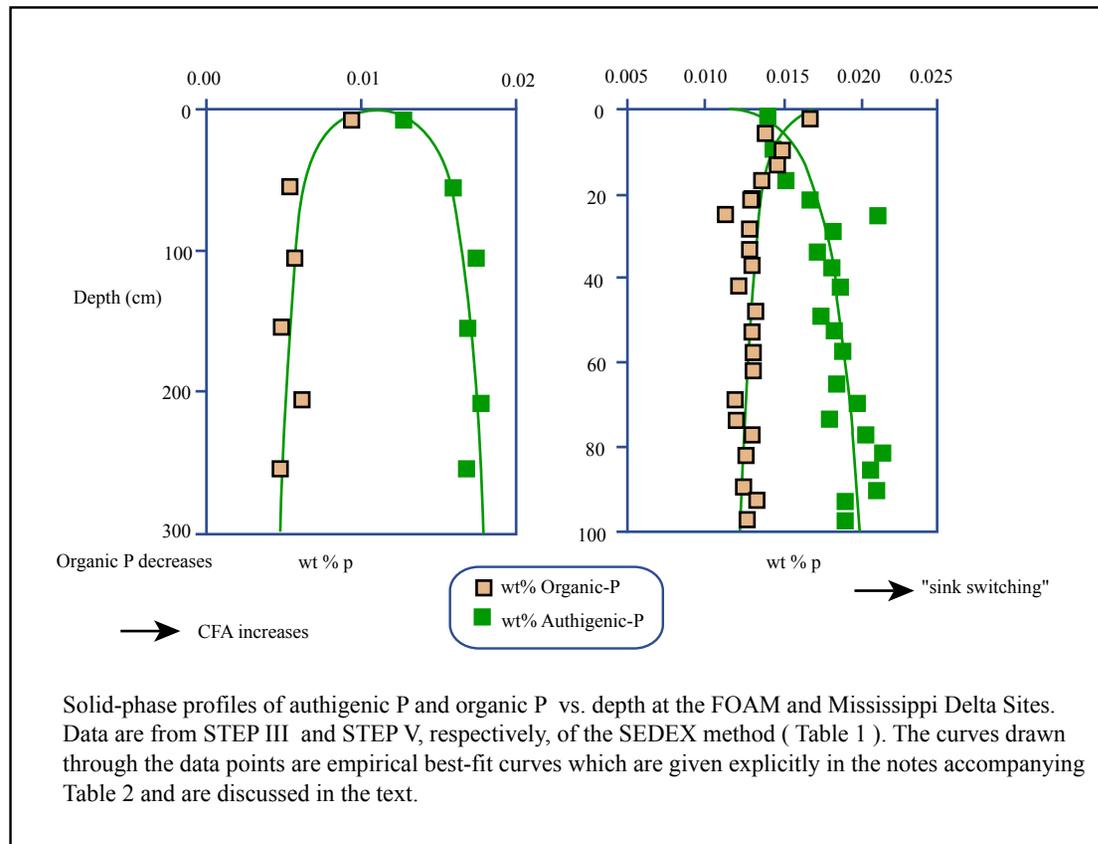


Figure by MIT OCW.

As $P_{org} \downarrow$ with depth, $CFA \uparrow =$ 'P sink switch'

Chemical nature of buried P in sediments

The precipitation of phosphate released from organic matter remineralization was also confirmed via pore water modeling

Predict phosphate pore water profile using a stoichiometric model of oxidation of sedimentary organic matter & measured profiles of ammonia

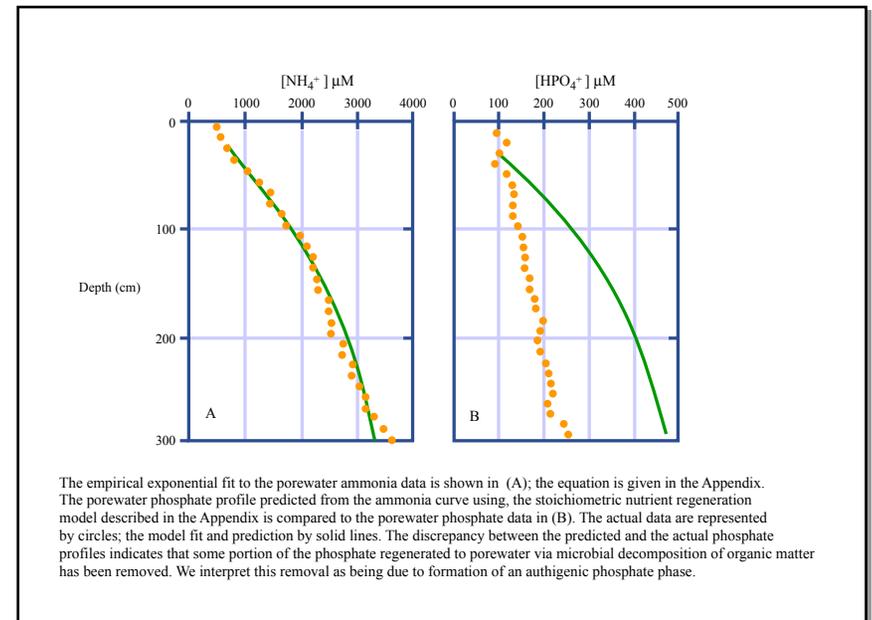


Figure by MIT OCW.

Far in excess = precipitation of an authigenic phosphate mineral

CFAs now seen as the main form of P present in deep-sea sediments

Organic P alone significantly underestimates total reactive P burial

P removal by hydrothermal processes

- Scavenging of phosphate from seawater by Fe oxides plumes occurs at hydrothermal vents

⇒ Fe fluxes from hydrothermal systems x mean P / Fe in the plume particles

Relatively small ($\sim 0.8 \times 10^{10}$ moles yr⁻¹)

- P is also removed via formation of authigenic apatite and adsorption on secondary Fe oxides during low temperature interactions between basalt & seawater

Larger ($\sim 3.0 \times 10^{10}$ moles yr⁻¹)

P residence time in the ocean

- Recognition of widespread CFA burial lead to significant revision of P residence time in the ocean:

Most recent estimates are 2-5 time higher than previous estimates = reduction in mean residence time in the ocean

Deep seawater P turnover:
 $2800 \times 10^{12} \text{ moles} / 0.038 \times 10^{12} \text{ moles yr}^{-1}$
 $\sim 74,000 \text{ years}$
 $\sim 15,000 - 30,000 \text{ years for new burial flux estimates}$

TABLE 3

The oceanic residence time of phosphorus

	Phosphorus burial ($10^{10} \text{ mol yr}^{-1}$)	$t_r^{(*)}$ (yr)
Modified estimates		
maximum end-member ^{*2}	18.5	16,000
minimum end-member ^{*3}	8.0	38,000
Previous estimate ^{*4}	3.8	80,000

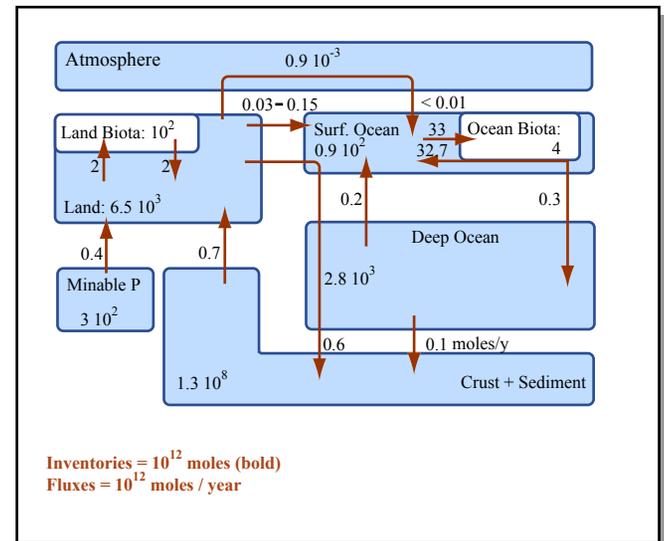


Figure by MIT OCW.

P inventory on glacial / interglacial timescales

- If phosphate is the ultimate limiting nutrient, changes in the oceanic P inventory would produce changes in the intensity of the biological pump, atmospheric CO₂, and O₂
- Reduced CFA burial at upwelling margins during glacial periods (Ganeshram et al., 2002), but this sink account for only ~10% of the total P removal

Location Area	P Burial	
	($\mu\text{mol cm}^{-2} \text{ yr}^{-1}$)	(10^6 km^2)
ETNP (off Mexico-Guatemala)*	0.3 to 1.6	0.5
ETSP (off Peru-Chile) ¹¹	0.8 to 6.3	0.2
Arabian Sea (off Oman and indo-Pakistan) ¹³	0.076 to 1.04	0.4
Southwest Africa (Namibian Shelf) ²³	2.8 to 1.04	0.03
West Australian Shelf ²⁴		<0.02
Global Phosphogenic P Burial**	1.2 x 10 ¹⁰ mol yr ⁻¹	

Figure by MIT OCW.

- If all other P sinks remained the same, P inventories would change very little (needs better constraints however)

Interactions between C, O, and P geochemical cycles

- P burial is more efficient when sediments are deposited under oxic conditions
- A potential negative feedback mechanism to control $[O_2]_{atm}$ over the Phanerozoic on Ma time-scales

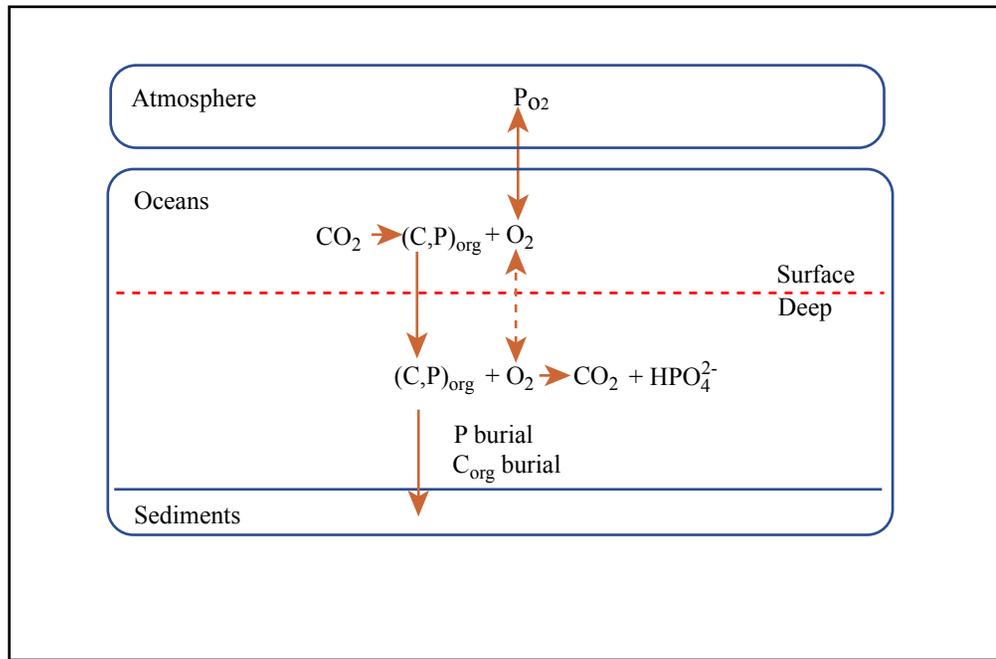


Figure by MIT OCW.

- If atmospheric O_2 ↓
- bottom water $[O_2]$ ↓
- P burial ↓
- Seawater P inventory ↑↑
- Export production ↑↑
- C_{org} burial ↑↑
- Atmospheric O_2 ↑↑