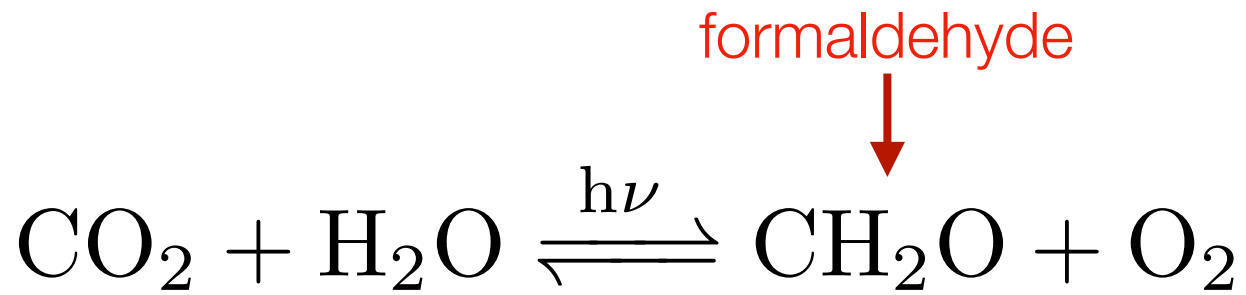


The Goal: a high total organic carbon (TOC) rock
need to produce OC, not dilute it, and preserve it from degradation
which process is most important?

Production

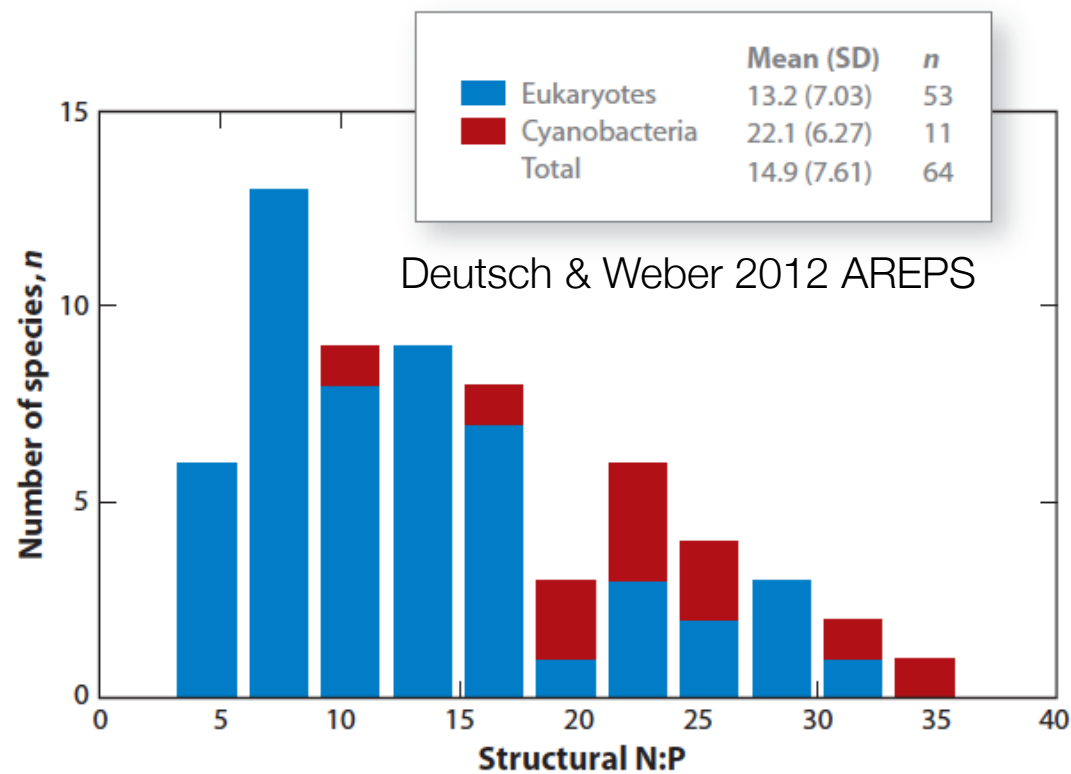


Production requires nutrients

fixed from atmosphere only in rocks

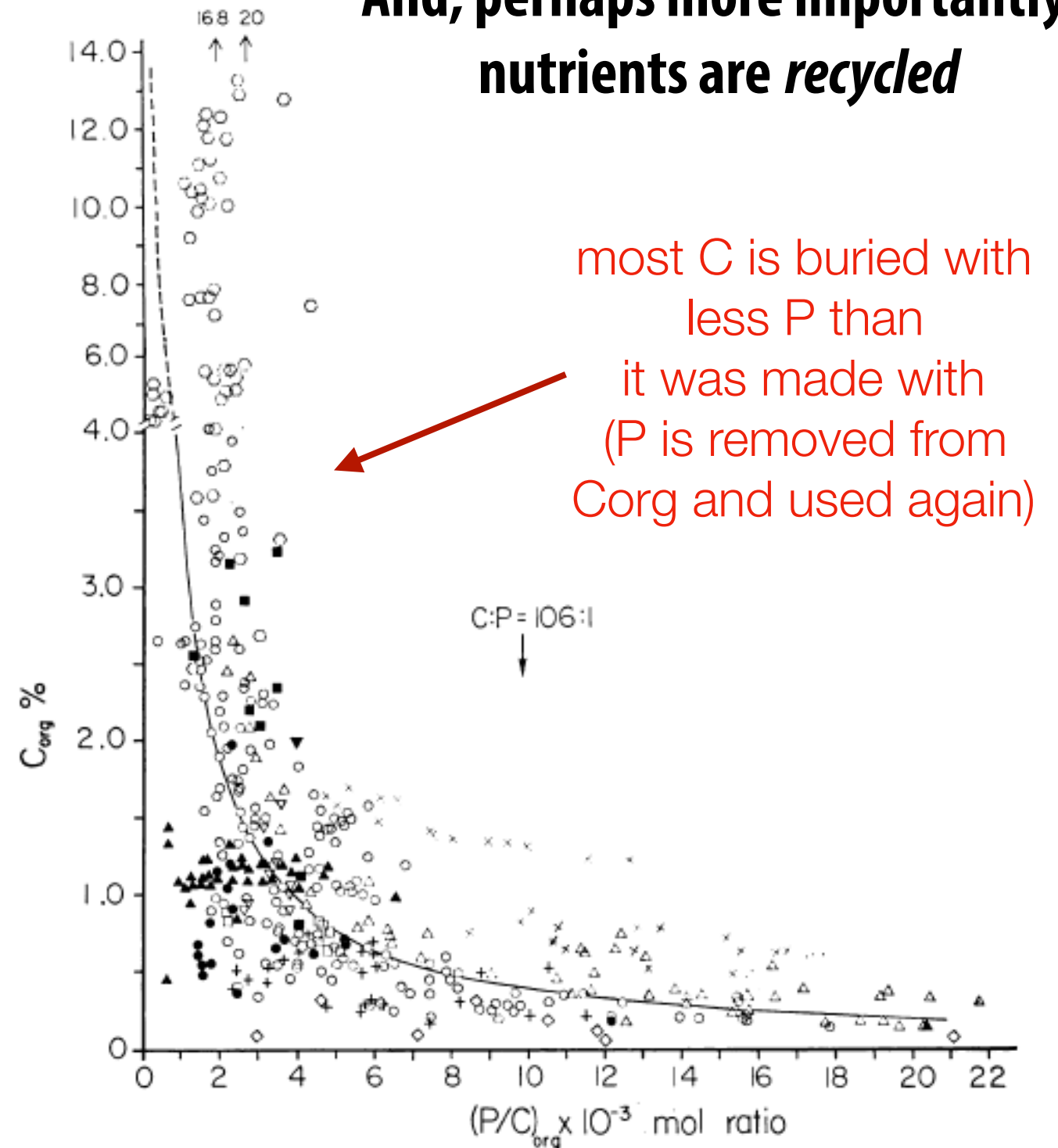
Redfield ratio: $\text{C}_{106}\text{N}_{16}\text{P}$

minor nutrients: Fe, S, Zn, Cu, etc.



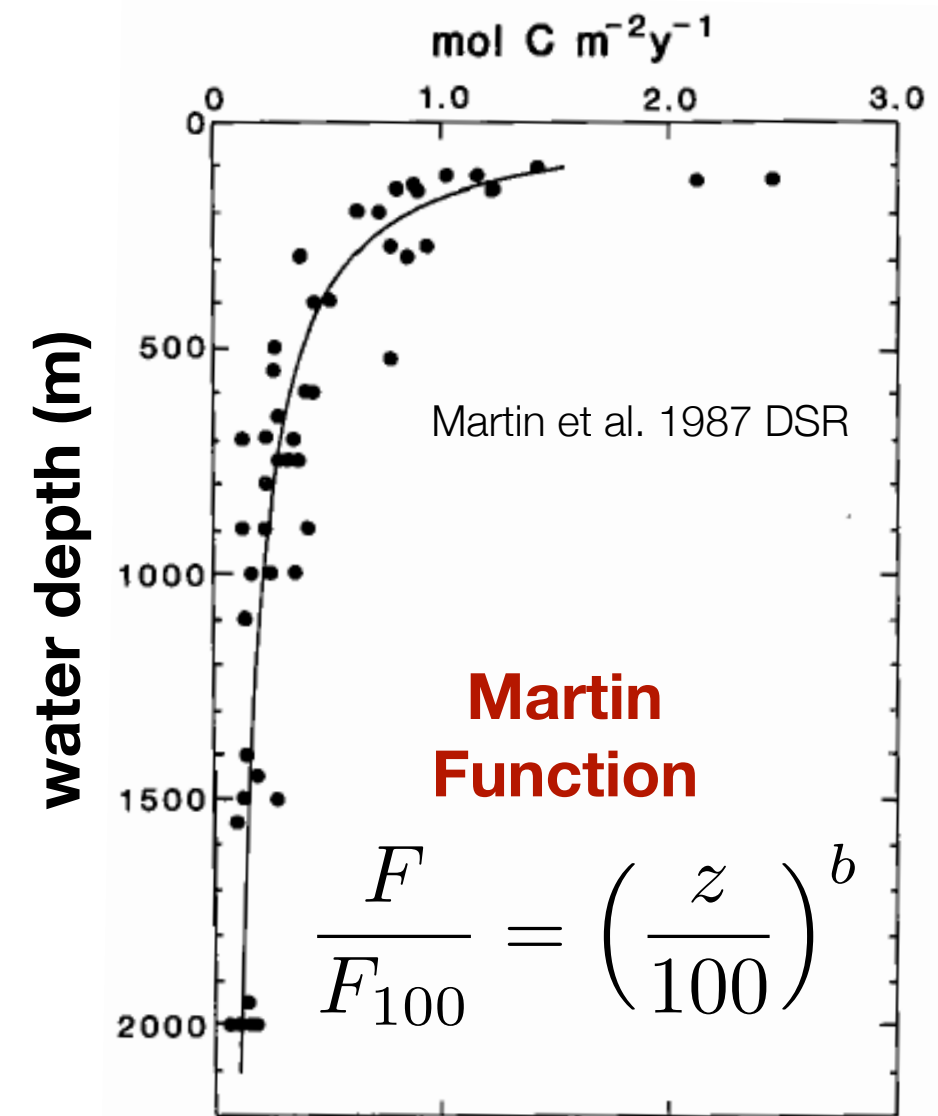
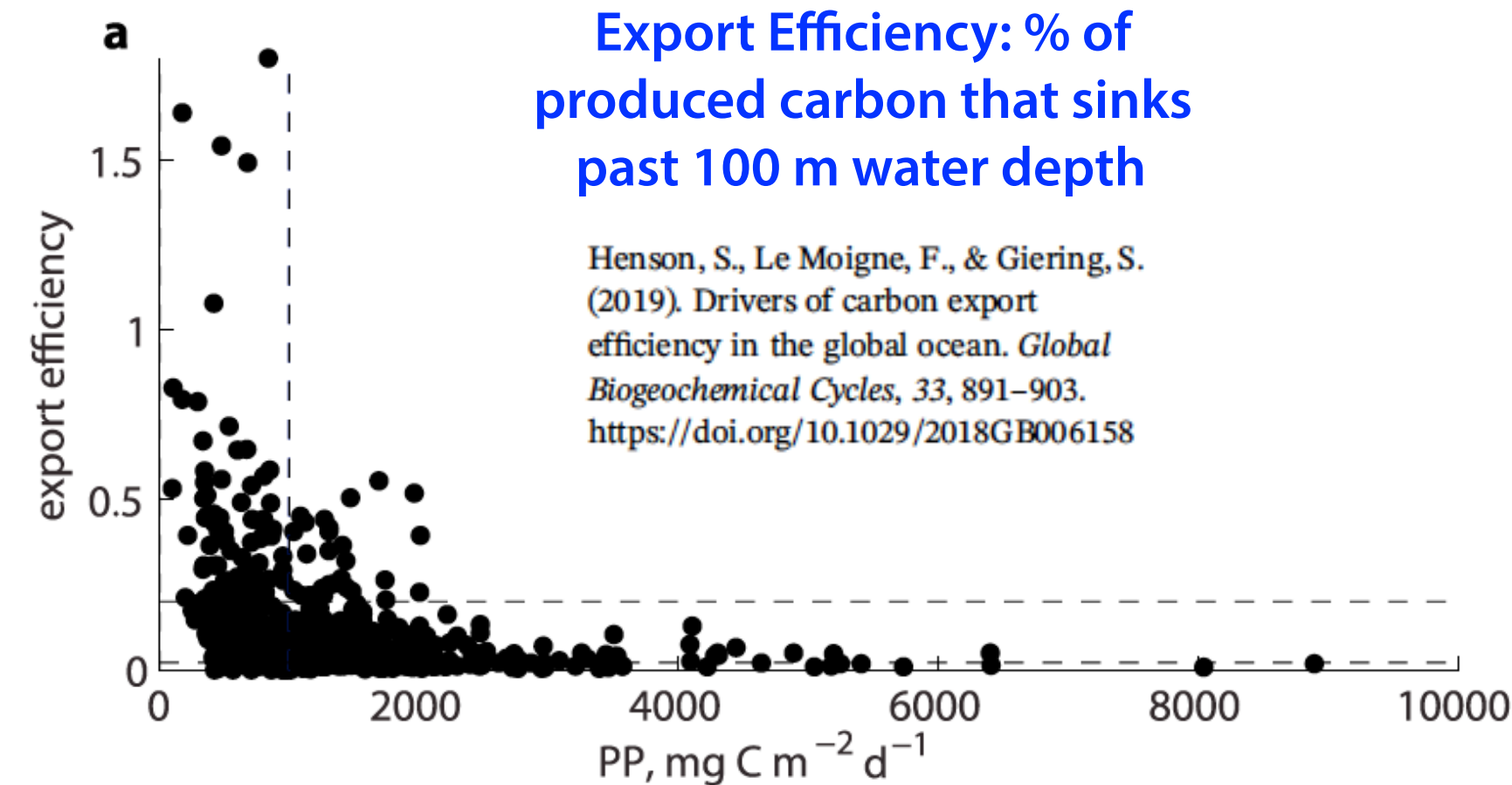
**but, nutrient demand is flexible
(context matters)**

**And, perhaps more importantly,
nutrients are *recycled***



Production

Of all of the TOC produced in the upper ocean, only a small fraction sinks past 100 m water depth



So, both recycling and export efficiency decouple OC production from external nutrient supply

what controls export efficiency?

Production

Ballast Hypothesis

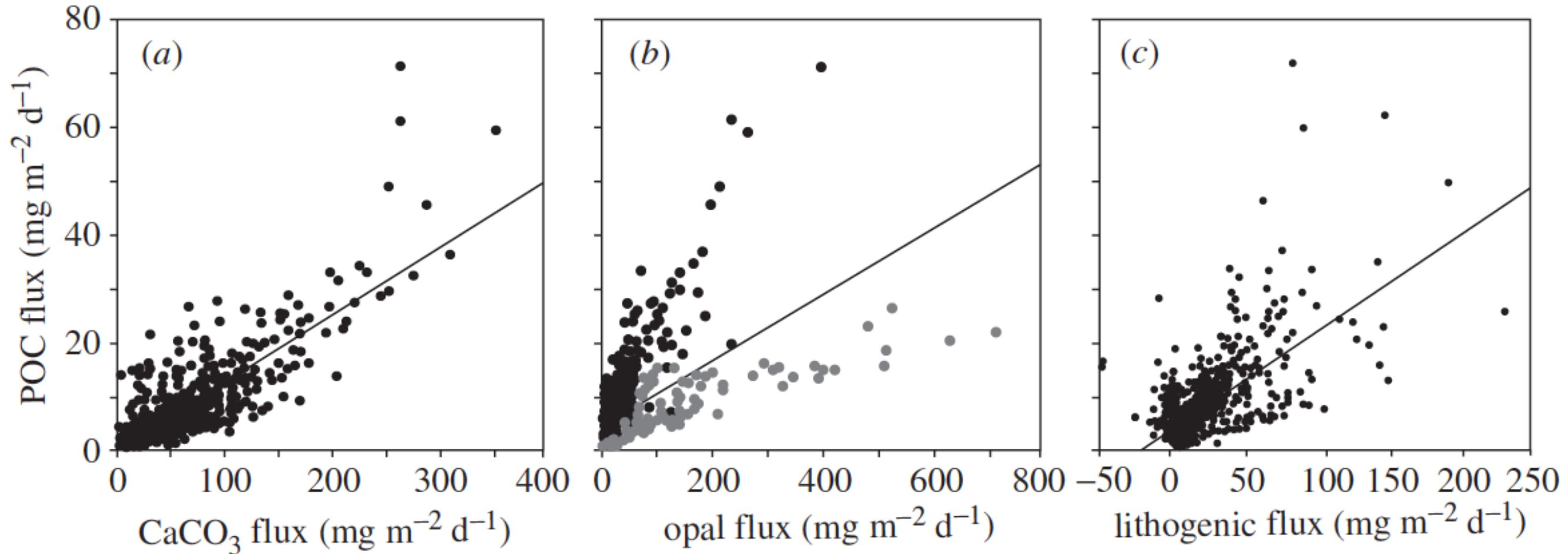
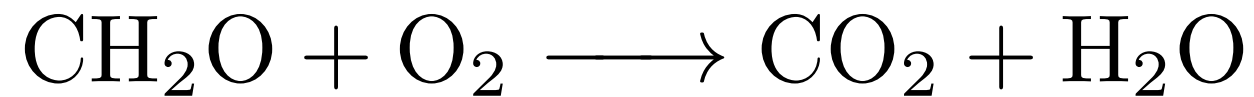


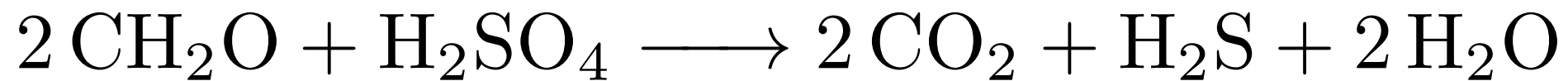
Figure 7. Scatter plots showing the correlation between POC flux and ballast flux below 1000 m from a global coverage of sediment traps. CaCO_3 is thought to be the most important transporter of POC to the deep sea. (a) $r = 0.829$, (b) $r = 0.595$, (c) $r = 0.536$; $P < 0.0001$. (Reproduced by permission from Klaas & Archer (2002). Copyright 2002 American Geophysical Union.)

Decomposition

Oxic Degradation

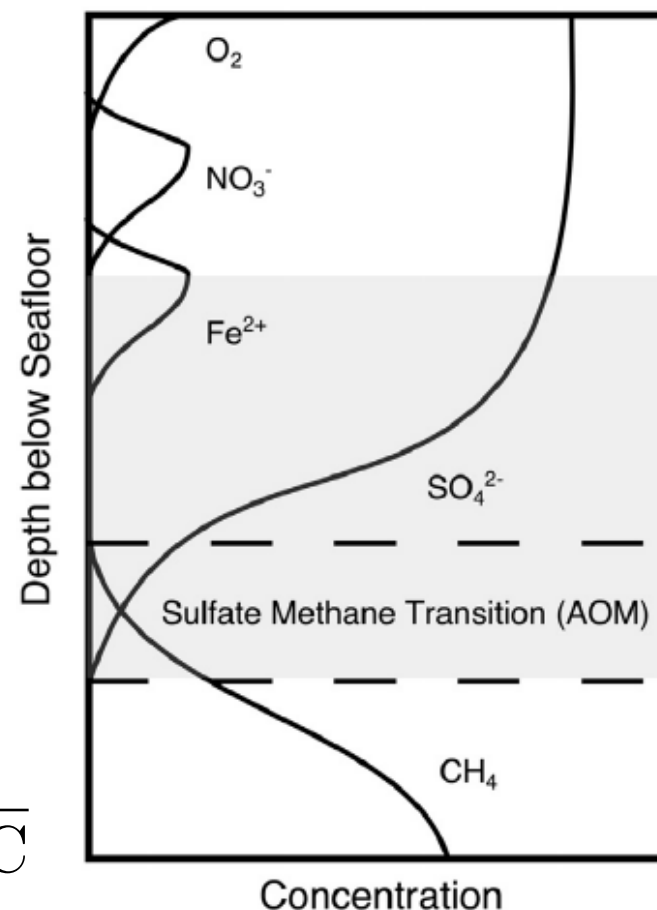
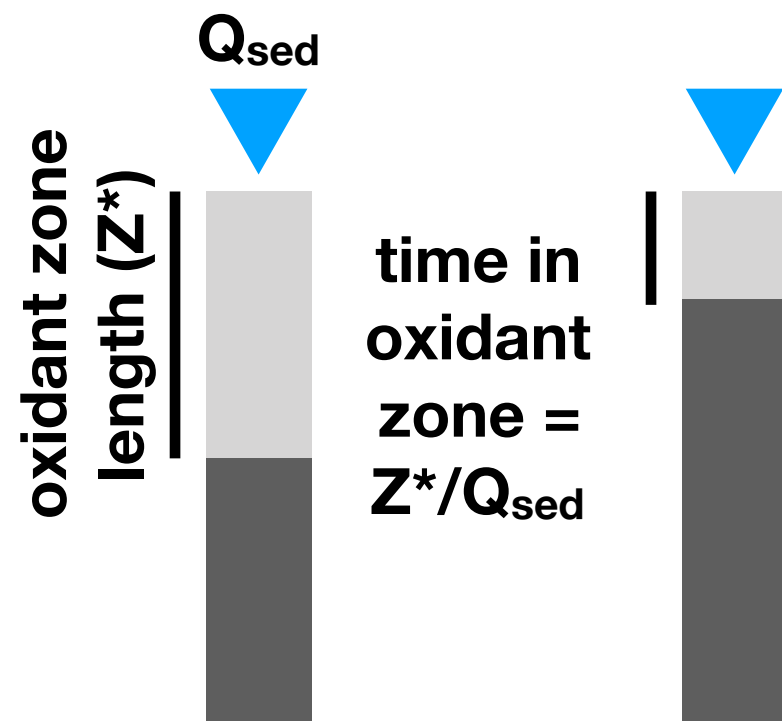


Anoxic Degradation



also works with Fe^{3+} , Mn^{4+} , NO_3^- , & disproportionation

Oxidants dissolved* in seawater degrade OC. So, to preserve OC, we need to bury it deeper than oxidant penetration depth quickly



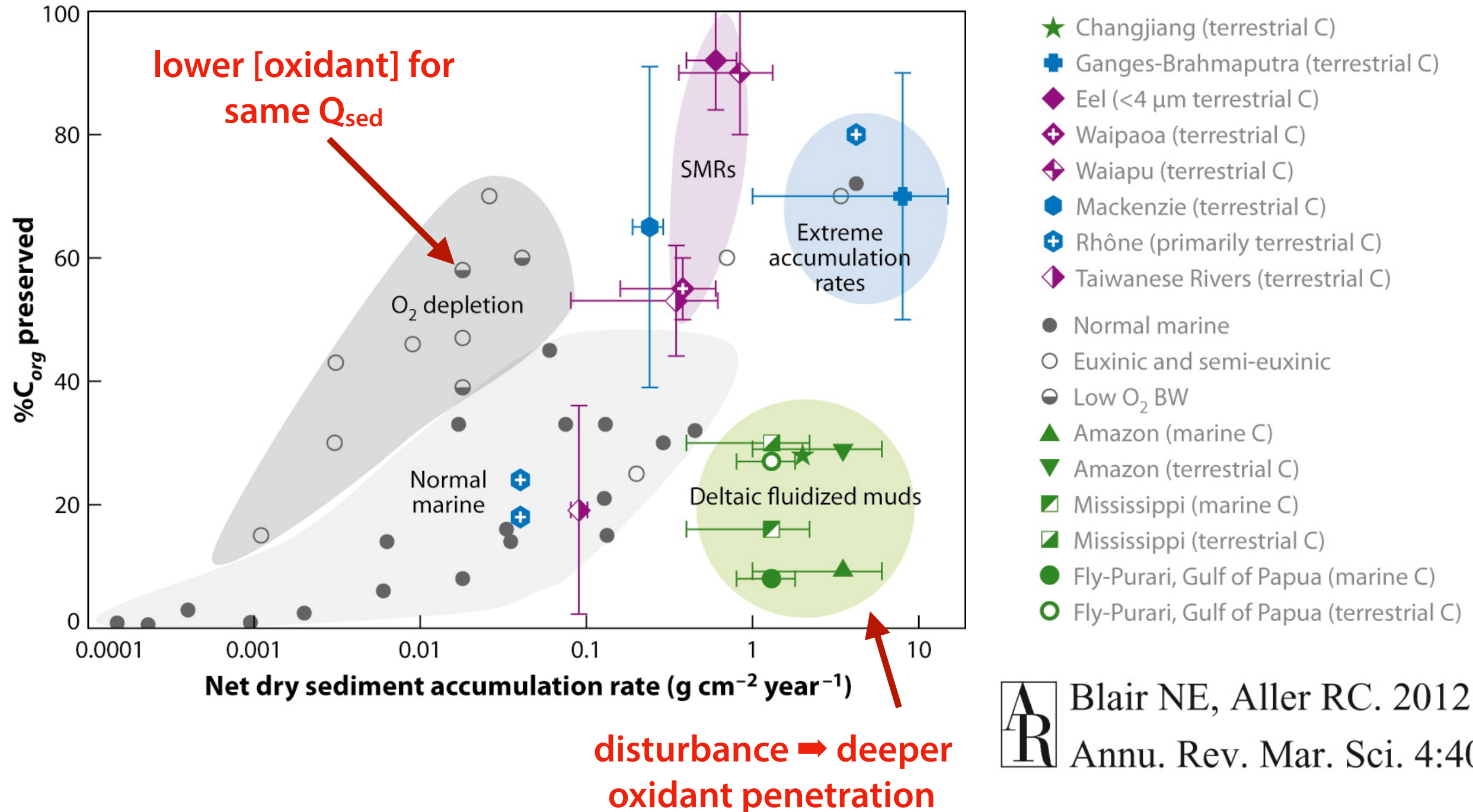
Reaction rates are complicated

- rates vary non-linearly with oxidant concentrations
- rates are different for different oxidants
- diffusive/advective oxidant transport
- Reactions energetically constrained (not all types of organic matter can react with all oxidants)

$$\text{Da} = \frac{\text{time in oxidant zone}}{\text{time required to oxidize OC}}$$

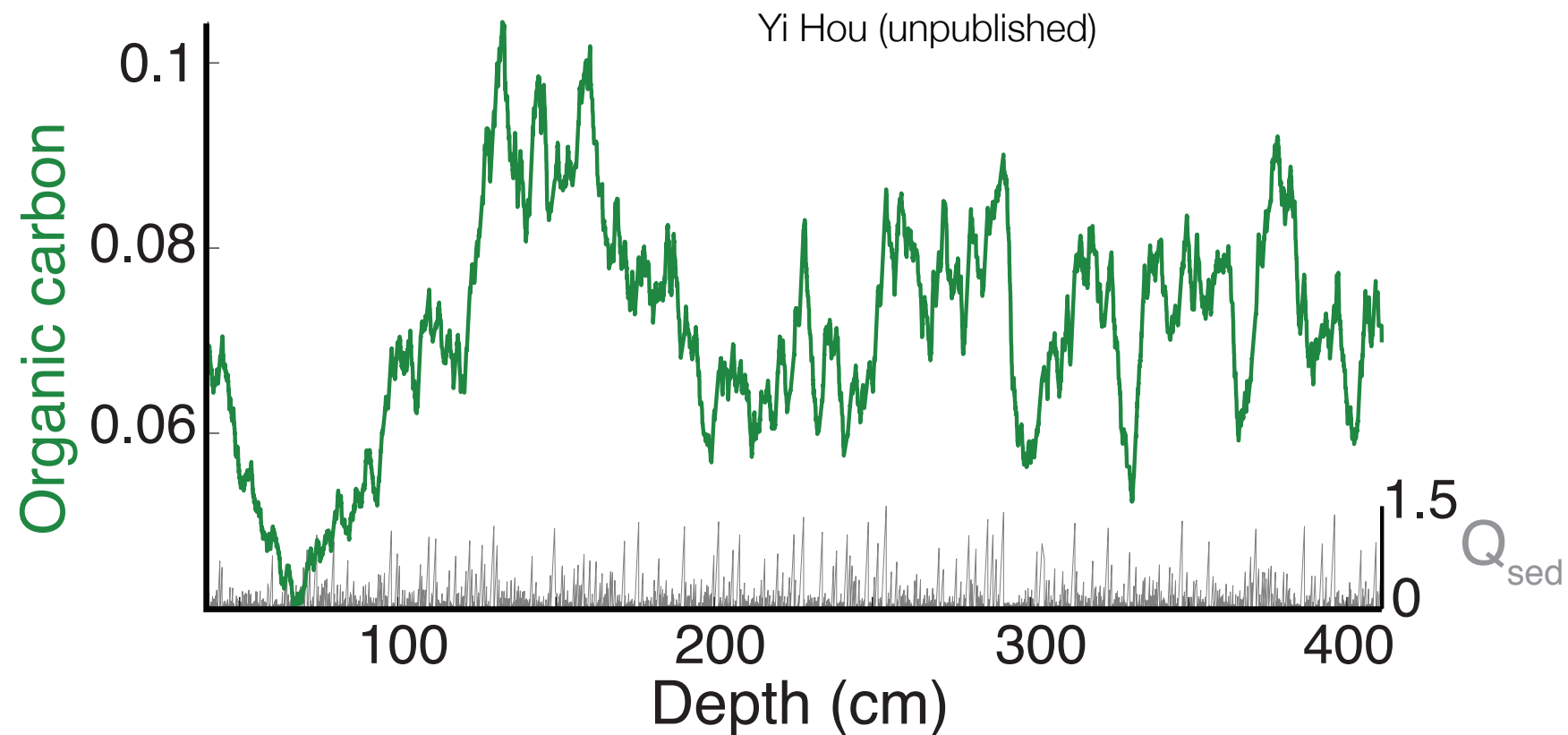
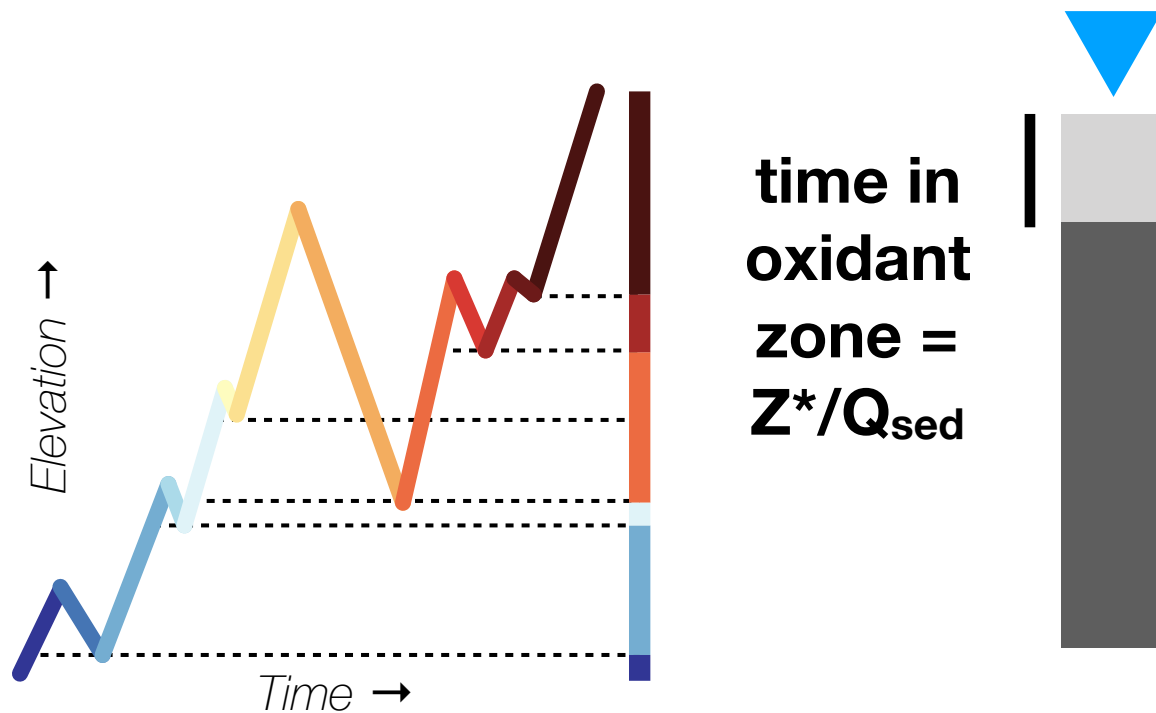
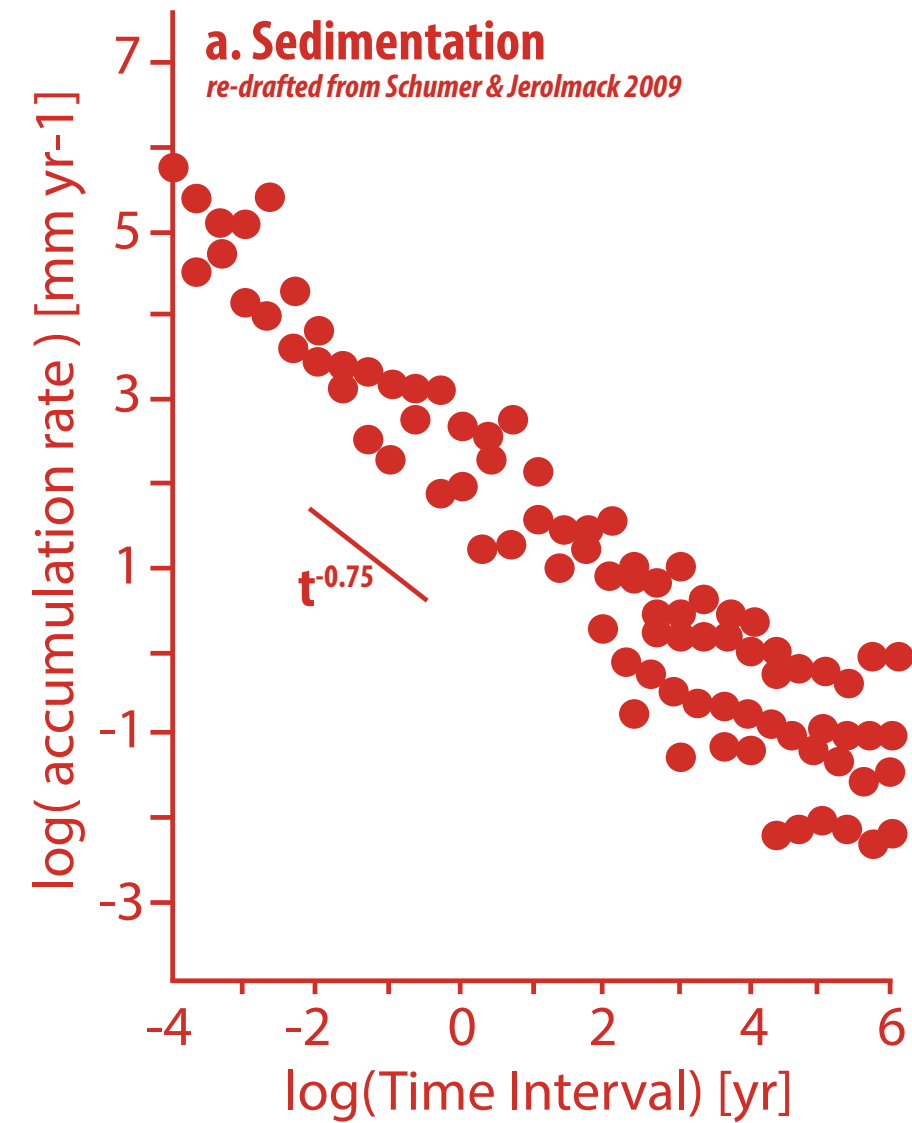
Decomposition

Of all of the TOC exported, only a small fraction is buried.
(small leak of a small leak)

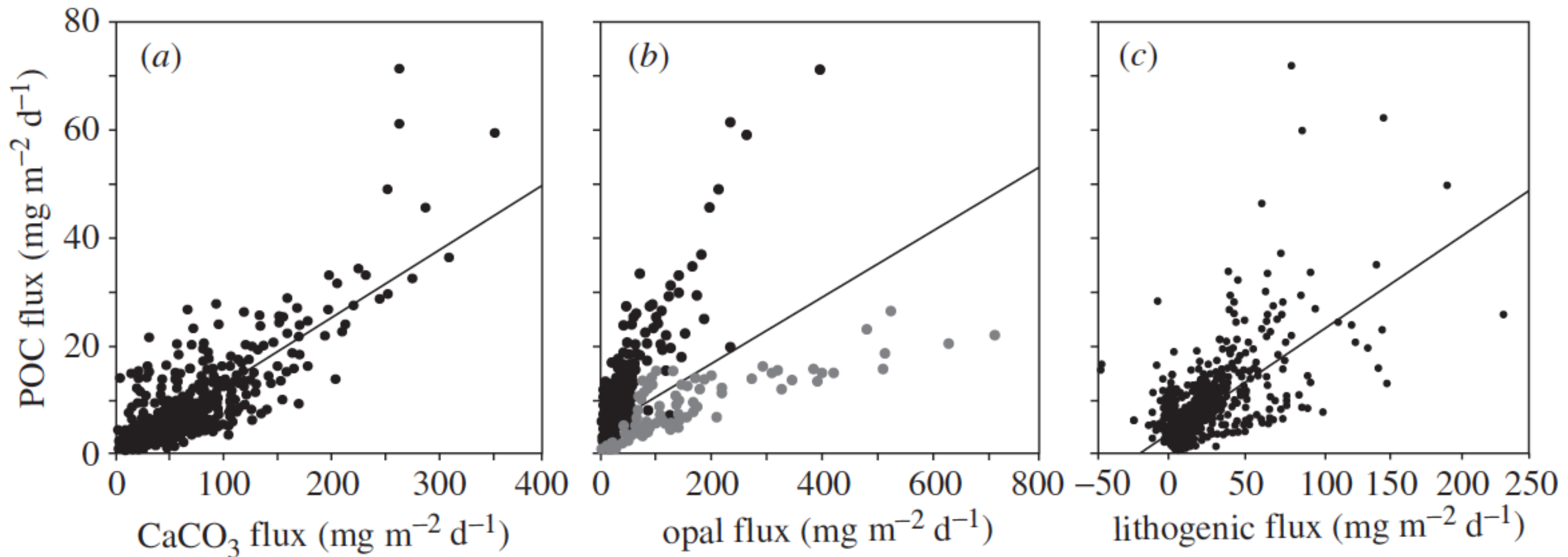
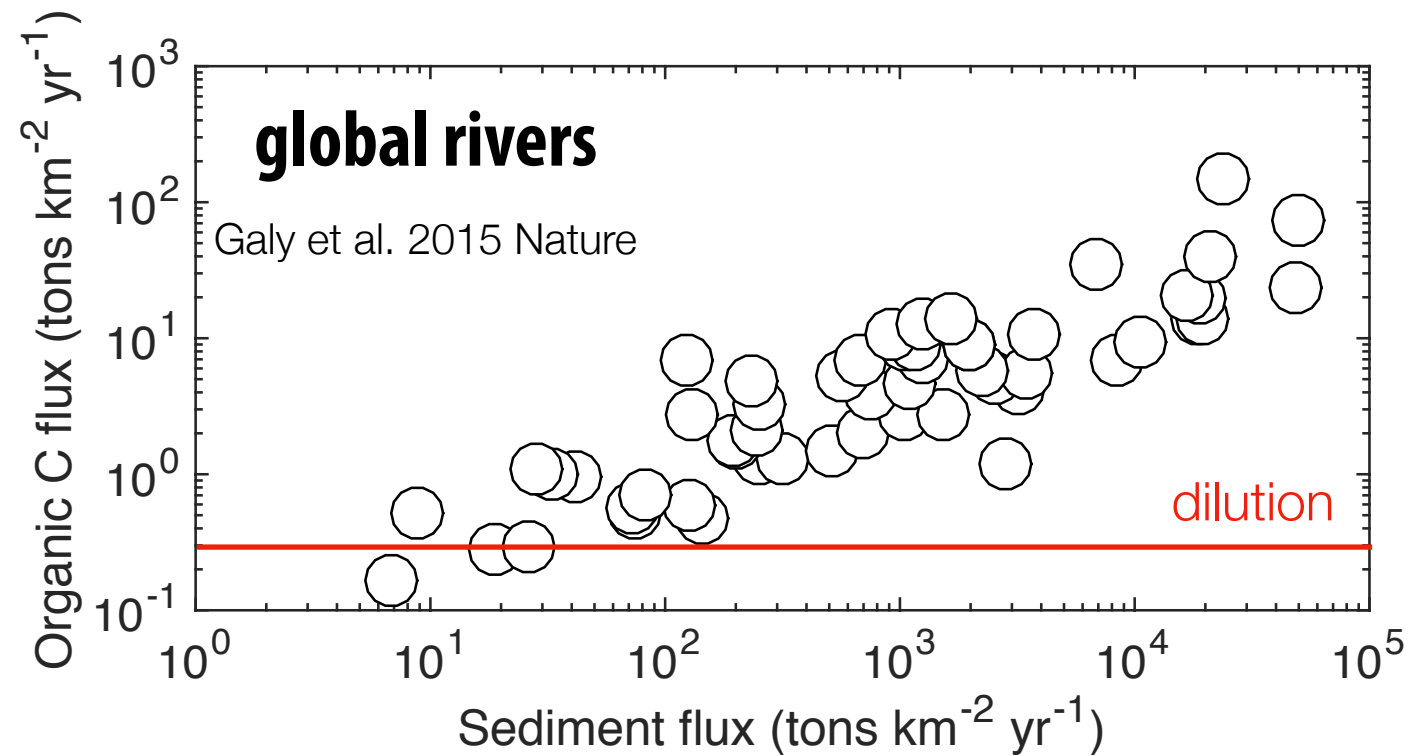


Blair NE, Aller RC. 2012.
Annu. Rev. Mar. Sci. 4:401

Decomposition *(what about variable sedimentation rates?)*



Dilution



Feedbacks

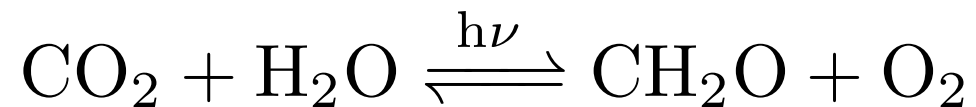
P recycling feedback (positive):

- P readily adsorbs to Fe³⁺ oxides
 - *adsorbed P is inaccessible (limit to recycling)*
- Increasing OC burial favors Fe³⁺ reduction
 - *Fe oxides converted to sulfides, releasing P*
 - *more efficient P recycling, more OC burial*
 - *invoked for OAEs*

Van Cappellen and Ingall 1996 Science

O₂ feedback (negative):

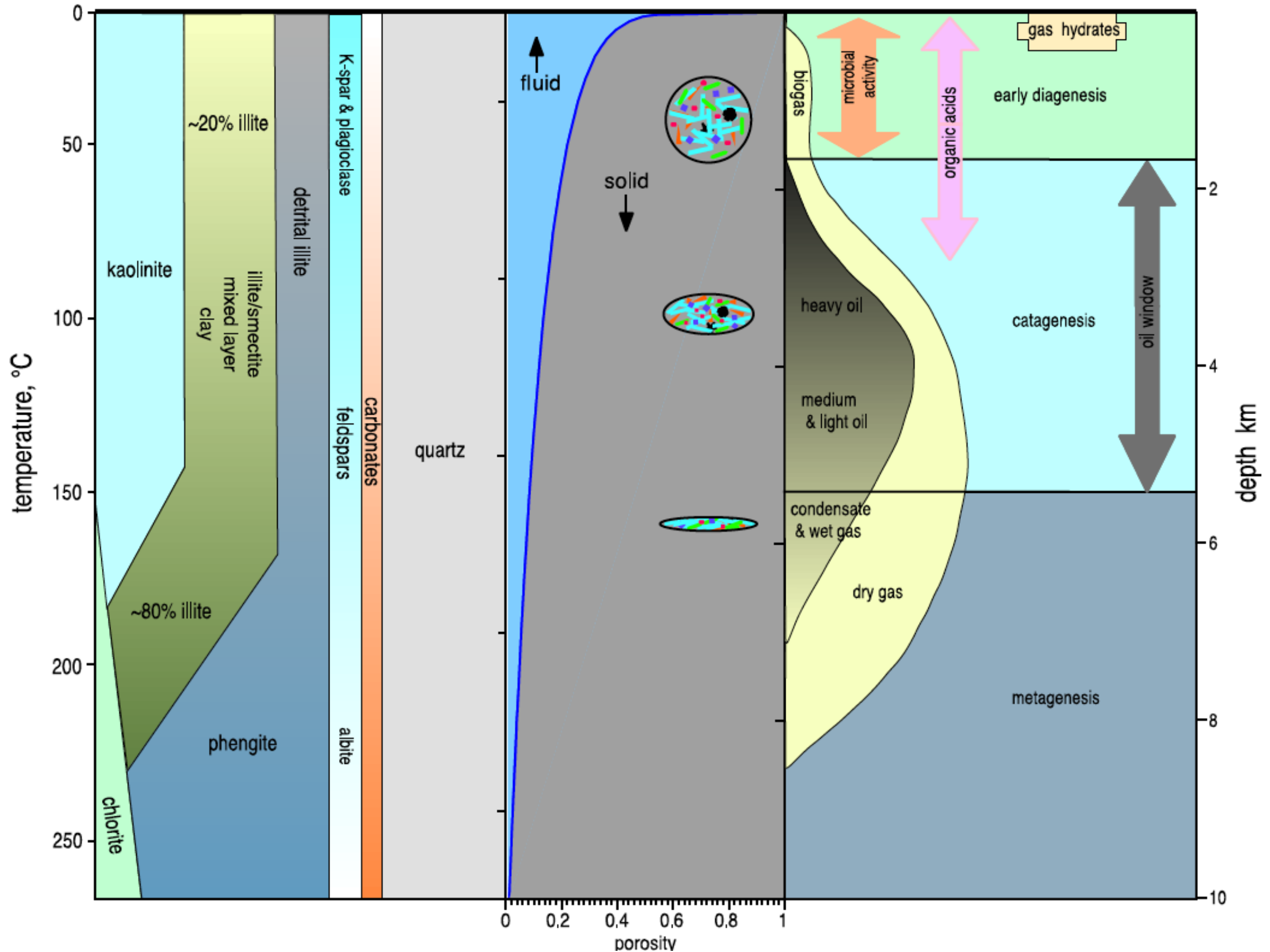
- Increasing net OC (and S) burial increases pO₂



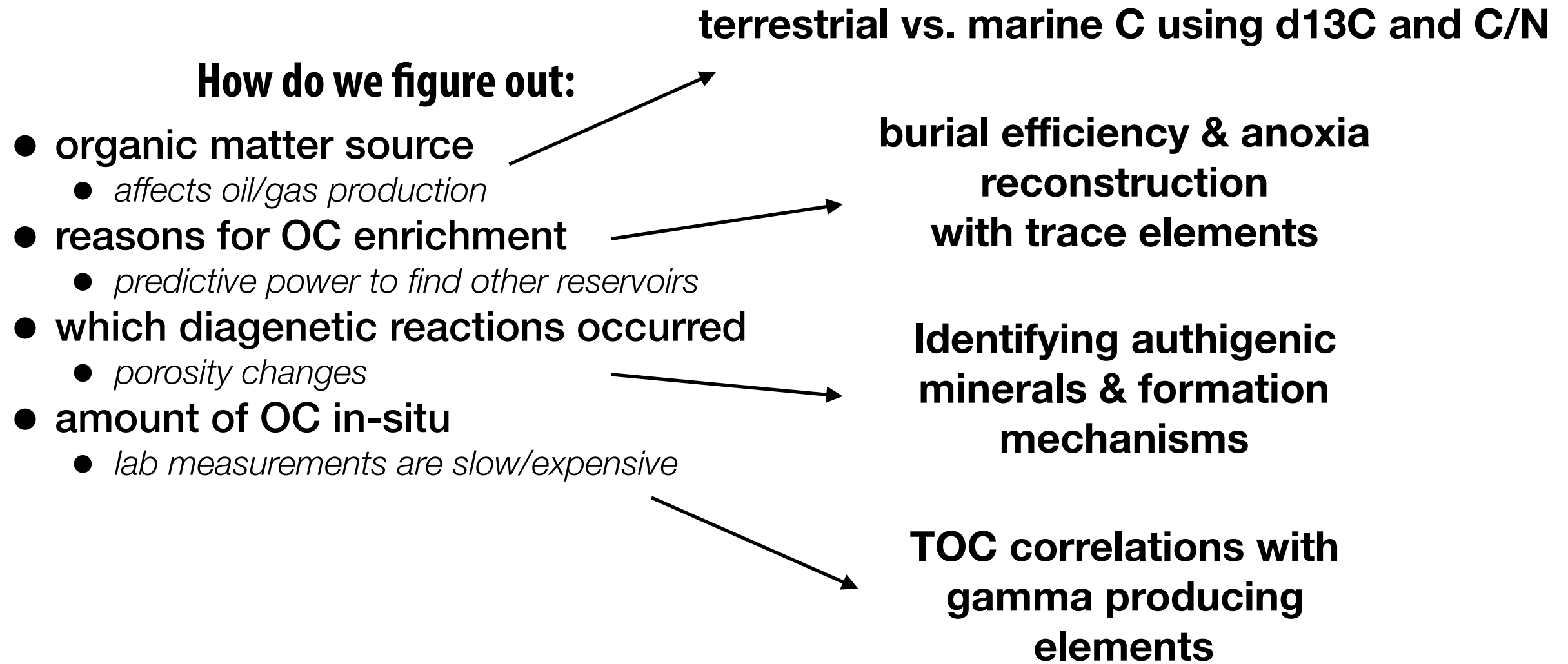
- *O₂ is dominant oxidant*
- Higher oxidant abundances decreases OC burial
 - *upper limit to atmospheric pO₂ thought to be spontaneous OC combustion*

Maturation, etc

Rimstidt et al. 2017 ESR



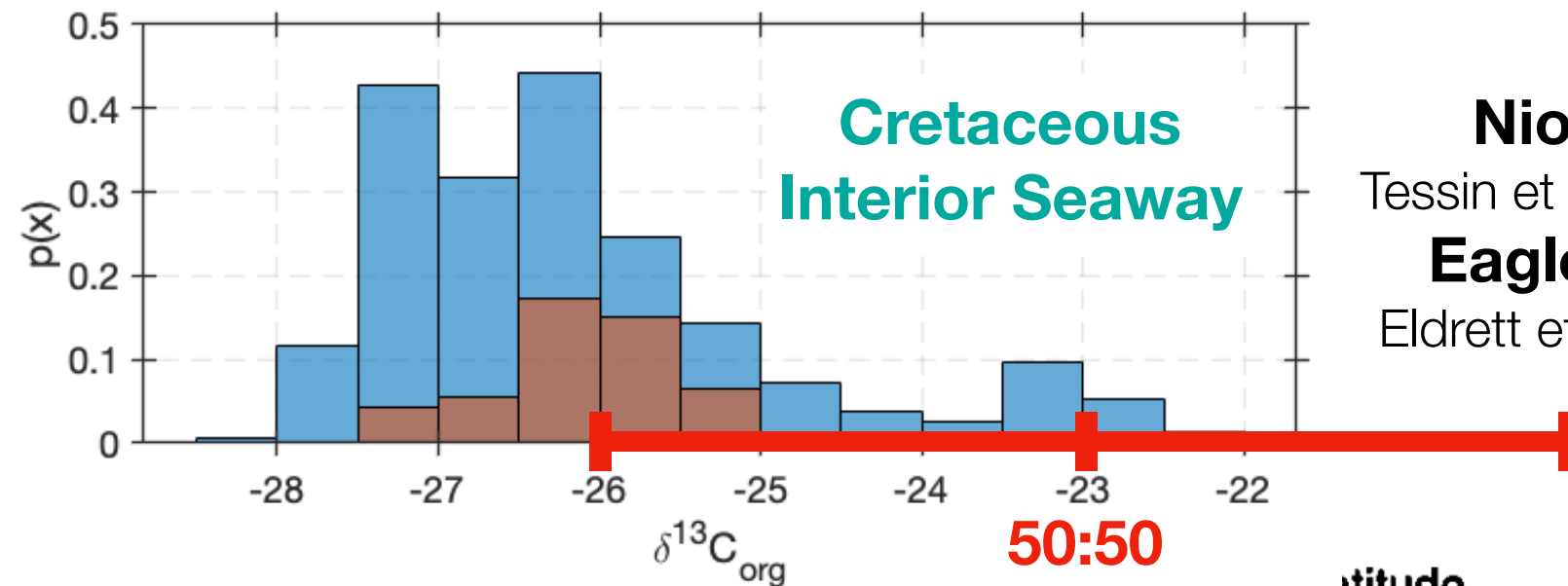
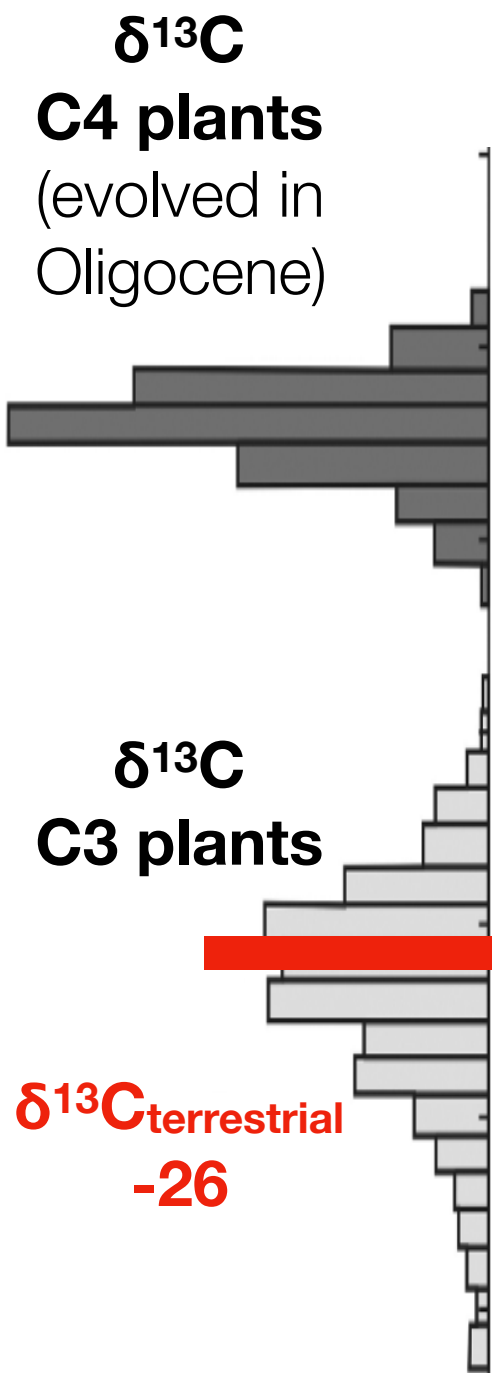
Toolkit



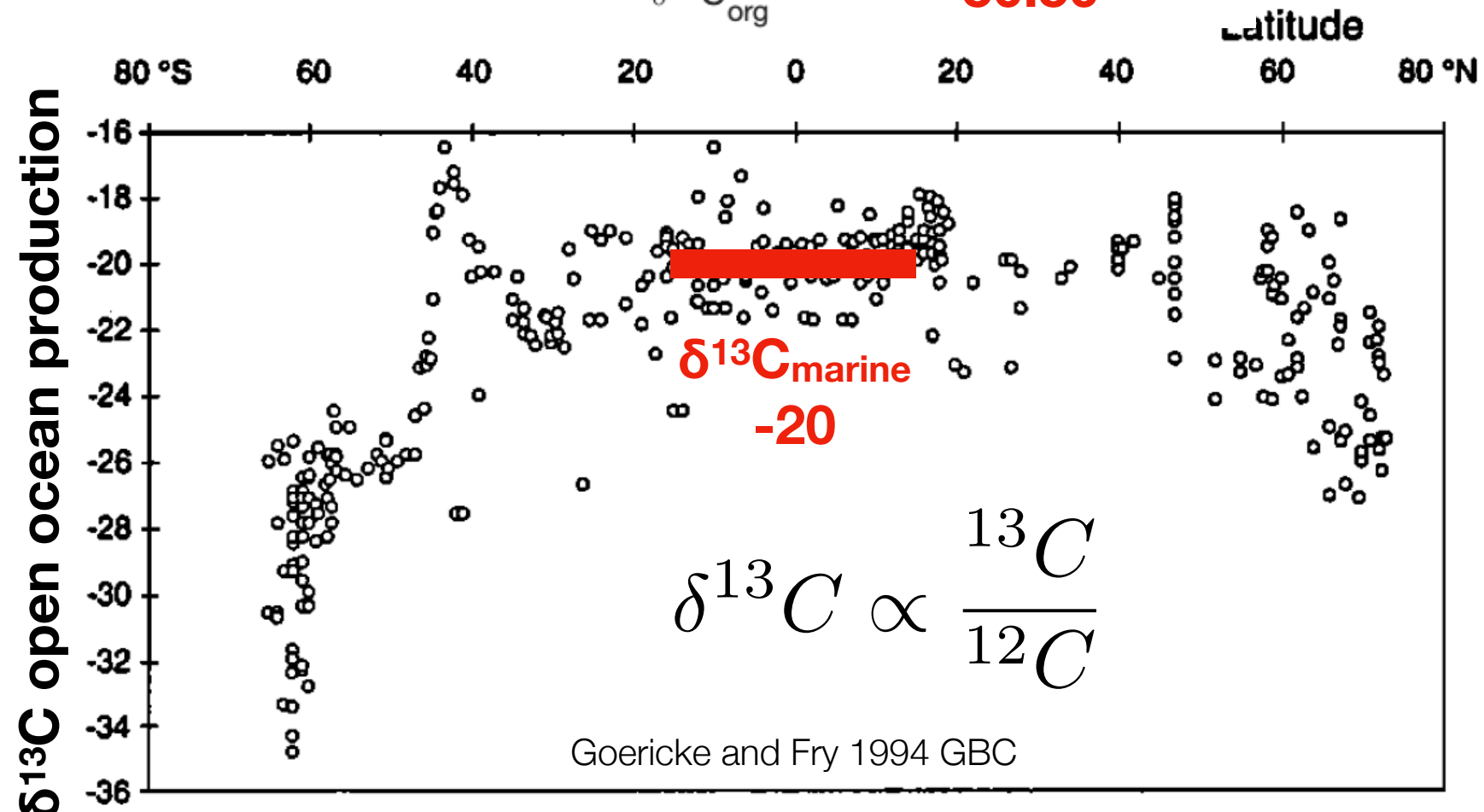
Terrestrial vs. Marine Carbon

$$\delta^{13}\text{C}_{\text{bulk}} = (f_{\text{marine}} \times \delta^{13}\text{C}_{\text{marine}}) + (f_{\text{terrestrial}} \times \delta^{13}\text{C}_{\text{terrestrial}})$$

$$1 = f_{\text{marine}} + f_{\text{terrestrial}}$$



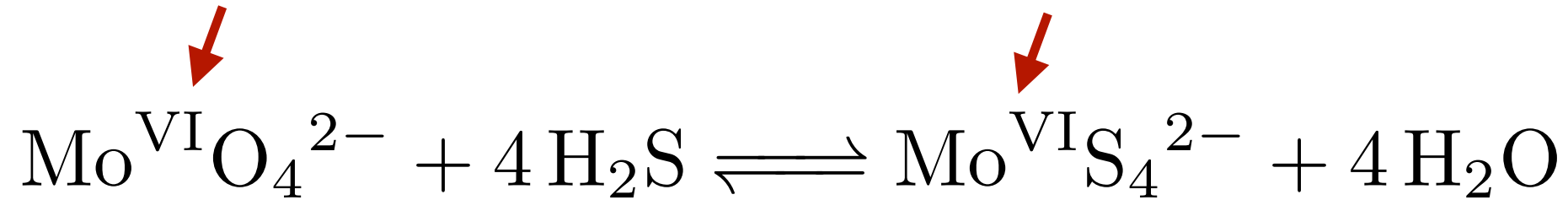
Niobara Fm
Tessin et al. 2015 PaleoO
Eagle Ford Fm
Eldrett et al. 2015 EPSL



Ancient Burial Efficiency

molybdate (likes to stay dissolved)

thiomolybdate (particle reactive)



- When enough TOC is buried that O_2 is consumed, SO_4 reduction starts
- The presence of H_2S changes Mo speciation (also applies to Re, U, Zn, etc) .
- Leads to removal of Mo from seawater and addition to sediments

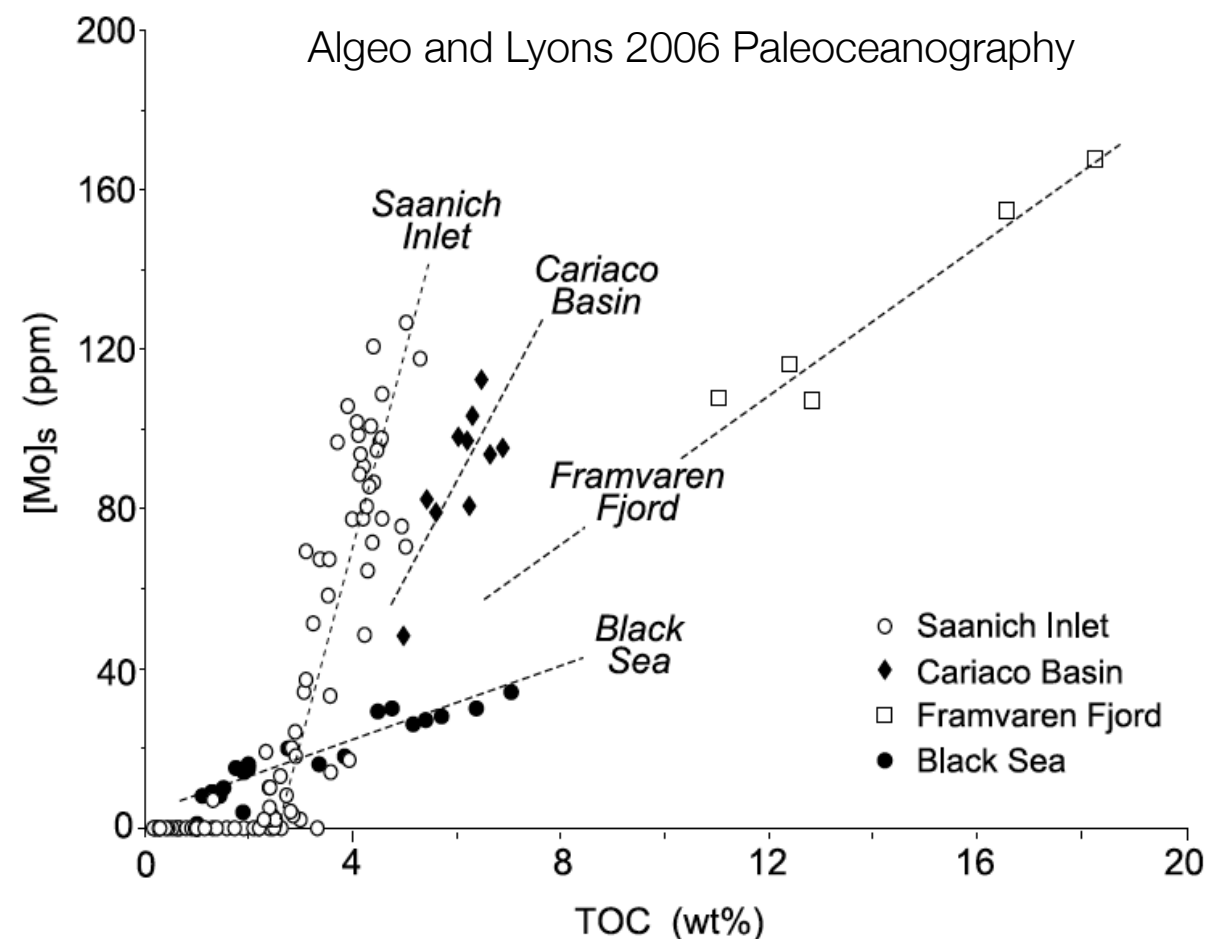
So, rocks with high Mo were likely deposited under anoxic (and sulfidic) conditions

What if authigenic carbonates form and dilute Mo? does that mean it wasn't anoxic?

Use Mo to Al ratio

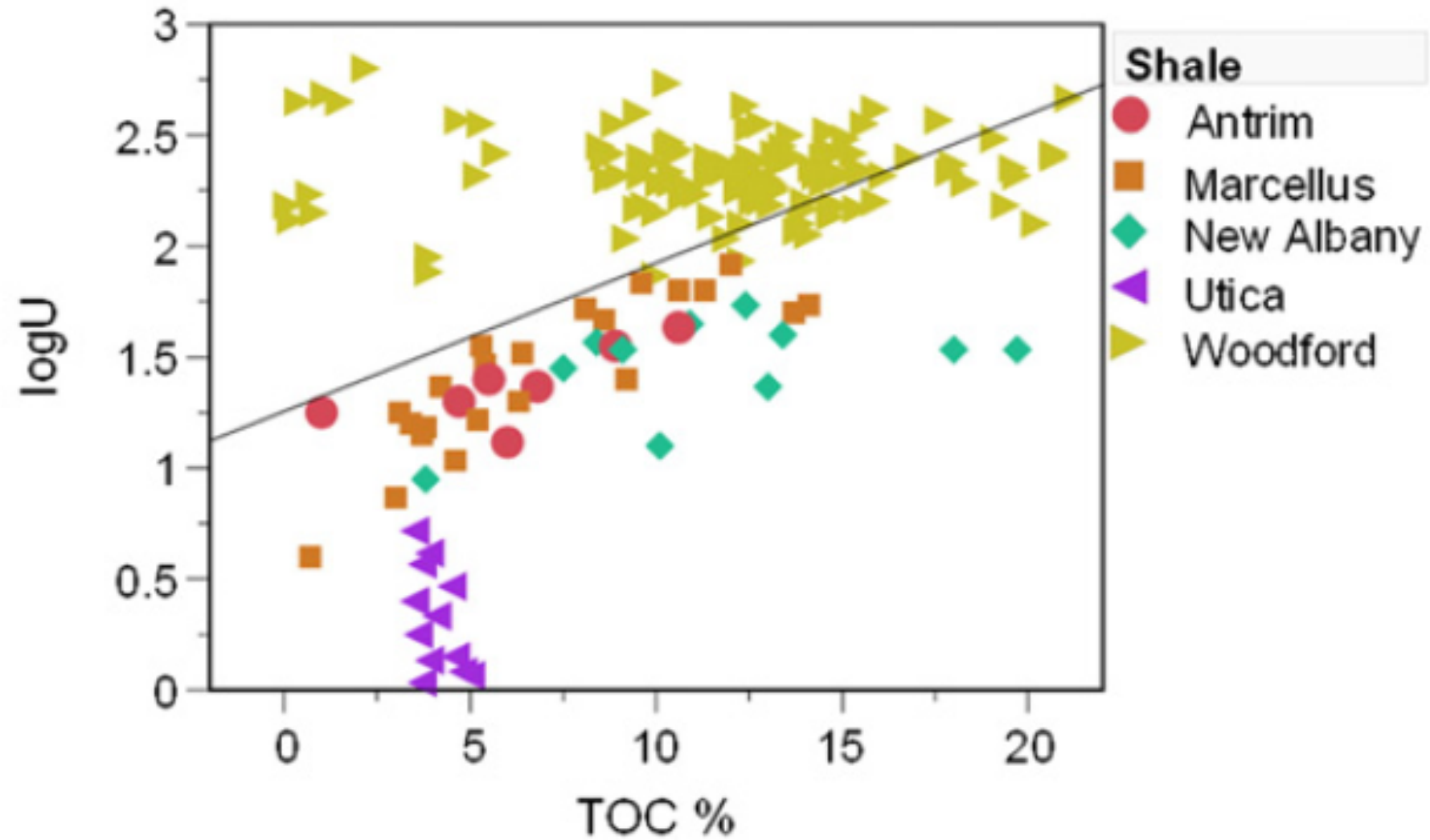
Detrital sediments carry Mo and Al, seawater scavenging adds only Mo since little Al dissolved in seawater and no redox effect for Al

What if seawater [Mo] changes?



TOC Correlations

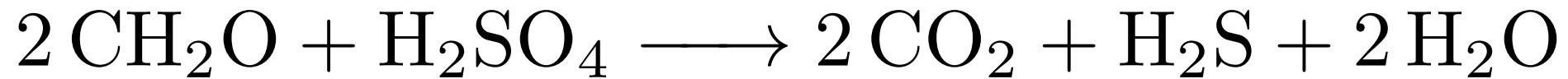
Chermak and Schreiber 2014 Int. J. Coal Geo.



TOC sometimes correlated with U, but not always. Why?

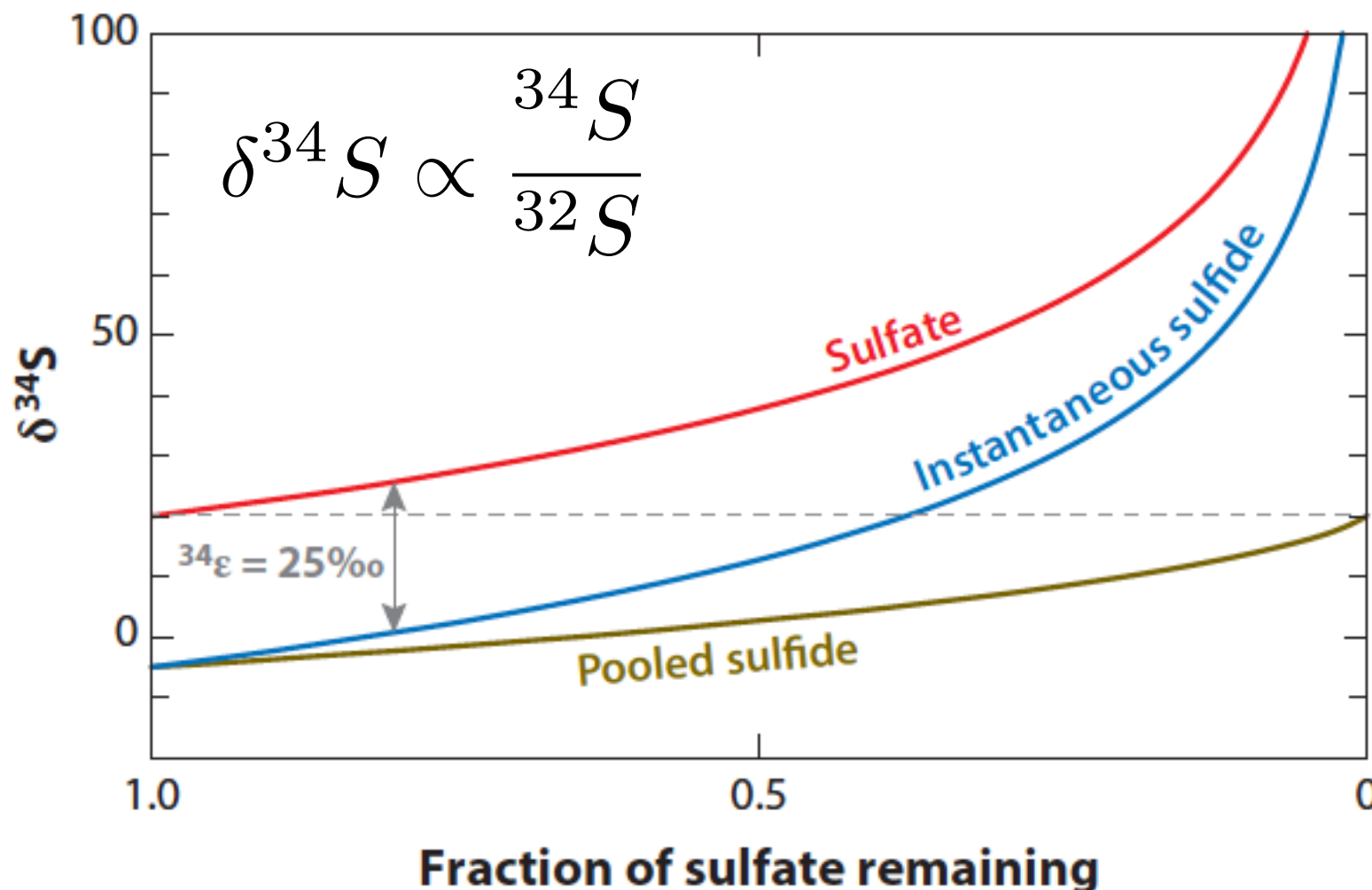
Authigenic Components of Marine Sediments

The formation of authigenic minerals in marine sediments directly relates to OC supply



↑ reacts to form FeS_2
(provided supply of reactive Fe)

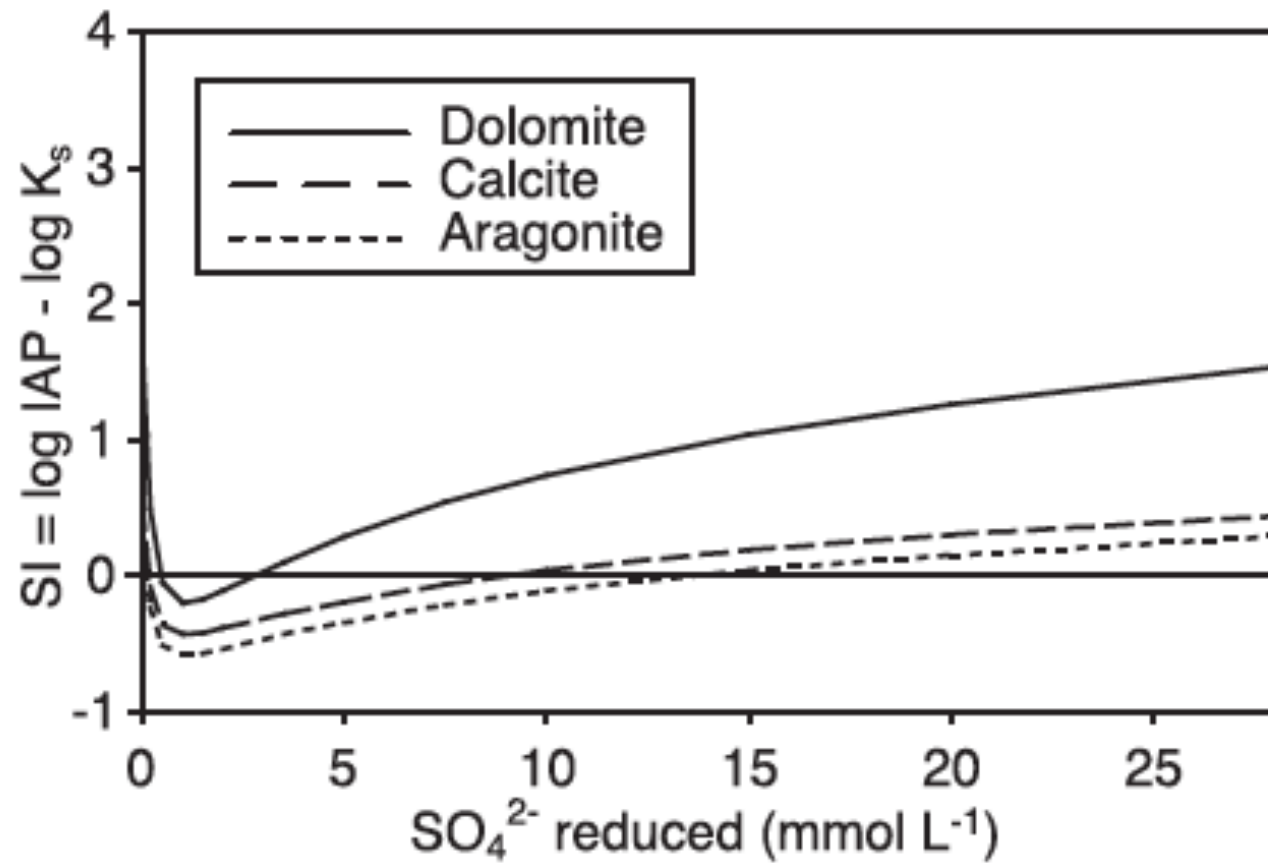
^{32}S preferentially reduced, but if all S is consumed, product (pyrite) has to have same isotopic composition as starting sulfate



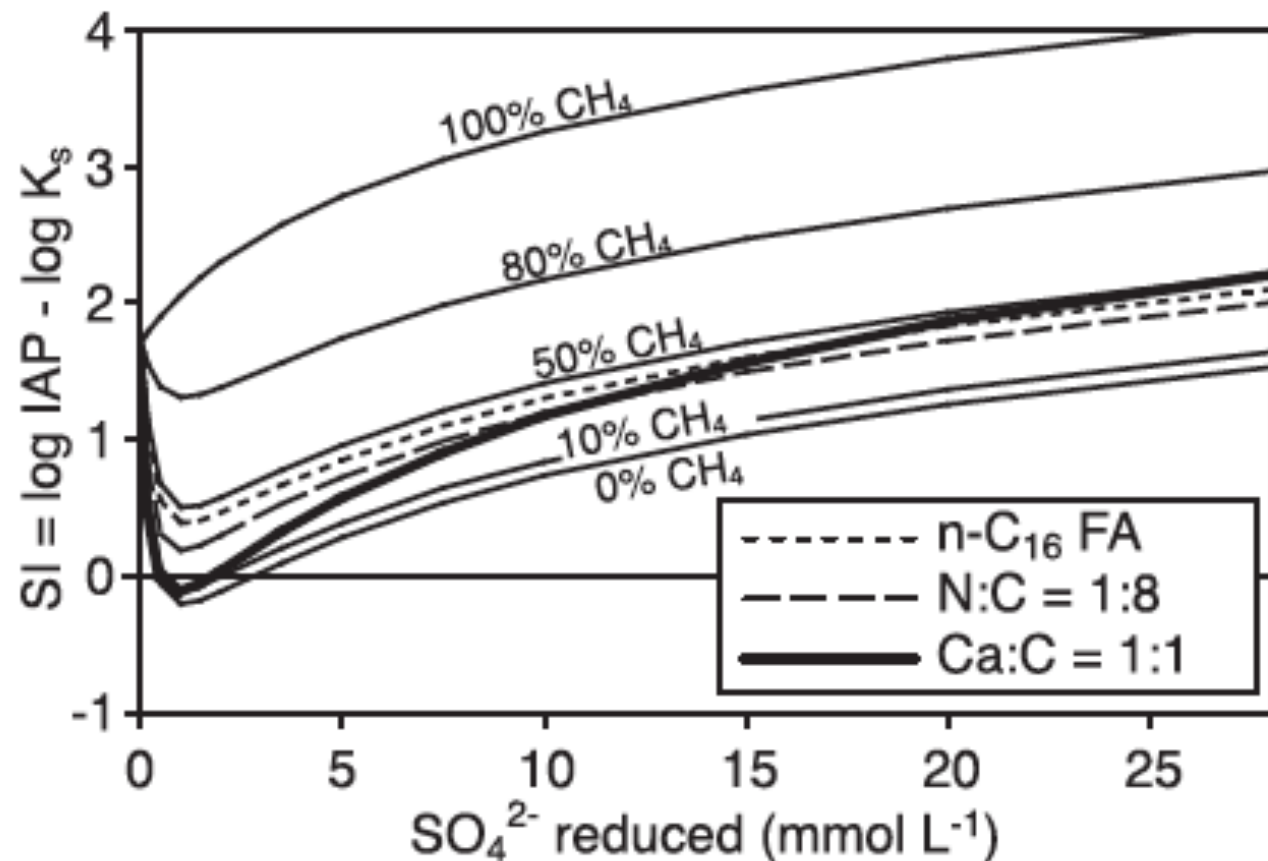
if bulk $\delta^{34}\text{S}_{\text{pyrite}} = \delta^{34}\text{S}_{\text{seawater}}$
and wide grain-scale range of $\delta^{34}\text{S}_{\text{pyrite}}$
restricted oxidant supply (closed system)

if bulk $\delta^{34}\text{S}_{\text{pyrite}} < \delta^{34}\text{S}_{\text{seawater}}$
and small grain-scale range of $\delta^{34}\text{S}_{\text{pyrite}}$
high oxidant supply (open system)

Sulfate reduction also affects authigenic carbonate formation



**need a lot of S reduction
to favor carbonate formation**



Unless methane is involved

Two opposing effects of sulfate reduction on carbonate precipitation in normal marine, hypersaline, and alkaline environments

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