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

And, perhaps more importantly, nutrients are recycled

\[ \text{Production requires nutrients} \]

fixed from atmosphere only in rocks

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

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

most C is buried with less P than it was made with (P is removed from Corg and used again)

\[ \text{CO}_2 + \text{H}_2\text{O} \xrightleftharpoons{h\nu} \text{CH}_2\text{O} + \text{O}_2 \]

but, nutrient demand is flexible (context matters)

Deutsch & Weber 2012 AREPS

Froelich et al. 1982 AJS
Of all of the TOC produced in the upper ocean, only a small fraction sinks past 100 m water depth.

Export Efficiency: % of produced carbon that sinks past 100 m water depth.


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

*what controls export efficiency?*
Figure 7. Scatter plots showing the correlation between POC flux and ballast flux below 1000 m from a global coverage of sediment traps. CaCO₃ 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**

\[ \text{CH}_2\text{O} + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O} \]

**Anoxic Degradation**

\[ 2 \text{CH}_2\text{O} + \text{H}_2\text{SO}_4 \rightarrow 2 \text{CO}_2 + \text{H}_2\text{S} + 2 \text{H}_2\text{O} \]

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.

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

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

Decomposition

lower [oxidant] for same $Q_{sed}$

$O_2$ depletion

Normal marine

Deltaic fluidized muds

SMRs

Extreme accumulation rates

disturbance $\Rightarrow$ deeper oxidant penetration

Changjiang (terrestrial C)
Ganges-Brahmaputra (terrestrial C)
Eel (<4 µm terrestrial C)
Waipaoa (terrestrial C)
Waiapu (terrestrial C)
Mackenzie (terrestrial C)
Rhône (primarily terrestrial C)
Taiwanese Rivers (terrestrial C)
Normal marine
Euxinic and semi-euxinic
Low $O_2$ BW
Amazon (marine C)
Amazon (terrestrial C)
Mississippi (marine C)
Mississippi (terrestrial C)
Fly-Purari, Gulf of Papua (marine C)
Fly-Purari, Gulf of Papua (terrestrial C)

Blair NE, Aller RC. 2012.
Annu. Rev. Mar. Sci. 4:401
Decomposition (what about variable sedimentation rates?)

- a. Sedimentation
  - Re-drafted from Schumer & Jerolmack 2009

- Elevation

- Time

- Decomposition

- Organic carbon

- Yi Hou (unpublished)
Dilution

Organic C flux (tons km$^{-2}$ yr$^{-1}$)

Sediment flux (tons km$^{-2}$ yr$^{-1}$)

Global rivers

Galy et al. 2015 Nature

(a) POC flux (mg m$^{-2}$ d$^{-1}$)

CaCO$_3$ flux (mg m$^{-2}$ d$^{-1}$)

(b) opal flux (mg m$^{-2}$ d$^{-1}$)

(c) lithogenic flux (mg m$^{-2}$ d$^{-1}$)
Feedbacks

P recycling feedback (positive):

- P readily absorbs to Fe$^{3+}$ oxides
  - *adsorbed P is inaccessible (limit to recycling)*
- Increasing OC burial favors Fe$^{3+}$ reduction
  - Fe oxides converted to sulfides, releasing P
  - more efficient P recycling, more OC burial
  - invoked for OAEs

Van Cappellen and Ingall 1996 Science

O$_2$ feedback (negative):

- Increasing net OC (and S) burial increases pO$_2$

\[
\text{CO}_2 + \text{H}_2\text{O} \xrightleftharpoons{h\nu} \text{CH}_2\text{O} + \text{O}_2
\]

- O$_2$ is dominant oxidant
- Higher oxidant abundances decreases OC burial
  - *upper limit to atmospheric pO$_2$ thought to be spontaneous OC combustion*
How do we figure out:

- organic matter source
  - affects oil/gas production
- reasons for OC enrichment
  - predictive power to find other reservoirs
- which diagenetic reactions occurred
  - porosity changes
- amount of OC in-situ
  - lab measurements are slow/expensive

terrestrial vs. marine C using d13C and C/N

burial efficiency & anoxia reconstruction with trace elements

Identifying authigenic minerals & formation mechanisms

TOC correlations with gamma producing elements
Terrestrial vs. Marine Carbon

\[ \delta^{13}C_{\text{bulk}} = (f_{\text{marine}} \times \delta^{13}C_{\text{marine}}) + (f_{\text{terrestrial}} \times \delta^{13}C_{\text{terrestrial}}) \]

\[ 1 = f_{\text{marine}} + f_{\text{terrestrial}} \]

\[ \delta^{13}C_{\text{marine}} = -20 \]

\[ \delta^{13}C_{\text{terrestrial}} = -26 \]

\[ \delta^{13}C_{\text{C4 plants}} \text{ (evolved in Oligocene)} \]

\[ \delta^{13}C_{\text{C3 plants}} \]

Niobara Fm
Tessin et al. 2015 PaleoO

Eagle Ford Fm
Eldrett et al. 2015 EPSL

Goericke and Fry 1994 GBC
Ancient Burial Efficiency

molybdate (likes to stay dissolved)  thiomolybdate (particle reactive)

\[
\text{Mo}^{VI} \text{O}_4^{2-} + 4 \text{H}_2\text{S} \rightleftharpoons \text{Mo}^{VI} \text{S}_4^{2-} + 4 \text{H}_2\text{O}
\]

- When enough TOC is buried that O\(_2\) is consumed, SO\(_4\) reduction starts
- The presence of H\(_2\)S 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 many 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.

\[
2 \text{CH}_2\text{O} + \text{H}_2\text{SO}_4 \rightarrow 2 \text{CO}_2 + \text{H}_2\text{S} + 2 \text{H}_2\text{O}
\]

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

\[\delta^{34}S \propto \frac{^{34}S}{^{32}S}\]

- If bulk \(\delta^{34}S_{\text{pyrite}} = \delta^{34}S_{\text{seawater}}\) and wide grain-scale range of \(\delta^{34}S_{\text{pyrite}}\) restricted oxidant supply (closed system)
- If bulk \(\delta^{34}S_{\text{pyrite}} < \delta^{34}S_{\text{seawater}}\) and small grain-scale range of \(\delta^{34}S_{\text{pyrite}}\) high oxidant supply (open system)

Fike et al. 2015 AREPS
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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