If the ocean is so efficient in remineralizing C and nutrients, why is C preserved at all in sediments?

Carbon preservation and the mystery of Mediterranean Sea Sapropels
**Sapropels**

- organic rich
  - (2-14% TOC)
- Periodic deposition
  - <1 cm to > 10 cm thick

**Nonsapropels**

- Very organic lean
  - (0.1% TOC)
- Most of the deposition
Sapropels

Any organic rich layer of sediment is called a sapropel. Sapropels in the Mediterranean Sea are very interesting however because the Med is one of the least productive bodies of water today, and sediments there are extremely depleted in organic carbon. A very long historical record of sapropel deposition was collected by the Ocean Drilling Program Legs 160 and 161 (see Initial reports…). Sapropels were first discovered in the Eastern Mediterranean Sea, but ODP found them to be synchronous in both basins. The shallowest sapropel is < 1m deep and can be sampled with a gravity core.
Organic carbon in Mediterranean Sea sediments

Calvert et al.
Global distribution of chlorophyll-a in September
Organic carbon in surface sediments of the Pacific Ocean

Calvert and Peterson 1998
Formation of Mediterranean Sea Sapropels
Enhanced productivity hypothesis

- Low production
- Nutrients
- Low carbon sediments
- High production
- Nile River at flood
- Sapropel deposition
Correlation between %OC and nitrogen isotopes in Mediterranean Sea sediments
Nitrogen isotopes in paleoproductivity and denitrification studies

<table>
<thead>
<tr>
<th>Central Gyres</th>
<th>Upwelling Zones and Polar Seas</th>
<th>Oxygen Minimum Zones</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low Nutrients</td>
<td>High Nutrients</td>
<td>Low Oxygen</td>
</tr>
<tr>
<td><strong>phytoplankton</strong></td>
<td><strong>phytoplankton</strong></td>
<td><strong>phytoplankton</strong></td>
</tr>
<tr>
<td>$\delta^{15}N = 5.9$ per mil</td>
<td>$\delta^{15}N &lt; 5.9$ per mil</td>
<td>$\delta^{15}N &gt; 5.9$ per mil</td>
</tr>
<tr>
<td>$\ NO_3^- \rightarrow N_{(organic)}$</td>
<td>$\ NO_3^- \rightarrow N_{(organic)}$</td>
<td>$\ NO_3^- \rightarrow N_2$</td>
</tr>
<tr>
<td>$\epsilon = 0$ per mil</td>
<td>$\epsilon = 6$ per mil</td>
<td>$\epsilon = 20$ per mil</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Deep Sea Nitrate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\delta^{15}N = 5.9$ per mil</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Carbon accumulation and the oxygen minimum zone of the Peru upwelling system
The effect of oxygen on carbon preservation in Maderia Abyssal Plain Turbidites

Before…  
During…  
and Voila!
The effect of oxygen on carbon preservation in Maderia Abyssal Plain Turbidites

Fig. 10. Depth distributions of (a) weight percent organic carbon, (b) combined mole percent of two nonprotein amino acids (β-alanine plus γ-aminobutyric acid), and (c) total pollen abundances (grains g⁻¹) in oxidized and unoxidized sediments from two cores of the f-turbidite collected at separate sites in the Madeira Abyssal Plain (data from Cowie et al., 1995; Keil et al., 1994b).
Formation of Mediterranean Sea Sapropels - anoxia hypothesis

low production

nutrients

low carbon sediments

Nile River at flood (fresh water)

low production

nutrients

anoxia

sapropel deposition
N isotope fractionation and early diagenesis

Early diagenesis operates like N uptake in biosynthesis. “Light” N is used first, so that sedimentary OM will get heavier (more enriched, or more positive) in N-15 as nitrogen is used during respiration.

However, this is not the case in anoxic systems because degradation proceeds via a different route. In anoxic sediments, there is little N fractionation with diagenesis.

If you measure the isotopic difference between the original N in biomass, and N that is left in sediments, the difference will be large (large fractionation factor in N uptake) in oxic sediments, whereas the difference will be small for anoxic sediments.
Correlation between %OC and nitrogen isotopes in Mediterranean Sea sediments

![Graph showing correlation between δ¹⁵N and organic carbon](image-url)
$\delta^{15}\text{N}$ in chlorophyll and sediment from Mediterranean Sea sapropels

Chlorophyll-$a$ is
the light harvesting
pigment in nearly
all marine algae

1) Chlorophyll (Chl) will record the N isotope value
of algal organic matter at the time of synthesis. The
isotopic difference between Chl and algal biomass is a
constant (5.9 per mil).

2) Diagenesis acts on total N, but will not change
the isotopic value of Chl.

4. If the isotopic difference ($\Delta\delta ^{15}\text{N}$) decreases during
sapropele formation, then N isotopic value is changing
due to diagenesis. If it is constant, then the value of N in
the water column is changing and $\Delta\text{N}15$ is set by changes in
productivity
$\delta^{15}$N in chlorophyll and sediment from Mediterranean Sea sapropels
What causes sapropels to form in the Mediterranean Sea? And more generally, what processes act to preserve carbon in marine sediments?

Enhanced productivity due to Inputs of nutrients?

or

Enhanced preservation due to Bottom water anoxia?

The productivity vs preservation debate
CP factor #1. The argument for productivity……
Relationship between % OC and sedimentation rate

% Organic Carbon vs. Sedimentation rate (mg cm$^{-2}$ y$^{-1}$)
Relationship between burial efficiency and sedimentation rate
Coupling and feedbacks between carbon and oxygen cycles

- tectonic degassing
- photosynthesis
- burial of organic carbon
Comparison of aerobic and anaerobic degradation

particulate organic matter

**anaerobic**

hydrolysis

**aerobic**

soluble organic matter

fermentation

LMW organic acids

Bacterial consortia

anaerobic respiration

CO₂

multicellular organisms
Effect of bottom water oxygen on burial efficiency
The effect of oxygen on carbon preservation in continental margin sediments

Hartnett et al. (1998) Nature v391, 572-574
The effect of oxygen has been refined somewhat to adjust for differences in exposure time, which is related to sedimentation rate (depth of $O_2$ penetration/sedimentation rate) = OET
Is carbon more efficiently respired under oxic or anoxic conditions?

Respiration of carbon in 0-1 cm and 17-20 cm sediment under oxic and anoxic conditions

Comparison of oxic and anoxic degradation rates in surface and deep sediments
Is carbon more efficiently respired under oxic or anoxic conditions?

Respiration of carbon in 0-1 cm and 17-20 cm sediment under oxic and anoxic conditions.

Comparison of oxic and anoxic degradation rates in surface and deep sediments.
Oxidation rate and the lability of organic carbon

(Lability of organic carbon (mol d$^{-1}$ g$^{-1}$))

(Anoxic rate/oxic rate)

17-20 cm
CP Factor #3  The composition of organic matter

Effect of chemical composition on organic matter degradation in sediments

Geopolymerization

- CCOOH
- HNH
- simple biochemicals

Selective preservation
- cellulose
- Lignin
  - HOOC
  - HOOC
  - HOOC
Was the composition of OM in anoxic sediments different than the OM in oxic sediments, thereby producing the observed difference?
Kinetics of organic matter degradation and the multi "G" model

\[ G = G_1 e^{-kt} + G_2 e^{-kt} + G_{NR} \]
Selective preservation of organic matter in sediments
If selective preservation occurs, then “old”, buried carbon should be recalcitrant. But is it?
Is the “G” model just and observational artifact?

\[
G = G_1 e^{-kt} + G_2 e^{-kt} + G_{NR}
\]
Productivity affects carbon burial efficiency.

Relatively more carbon is buried under anoxic than oxic conditions.

Bigger molecules are degraded more slowly than smaller molecules.

The faster you bury carbon, the more likely it is to stay buried.

The Carbon Preservation Quiz!

Figure by MIT OCW.
Carbon preservation summary

Ocean is >99.5% efficient at recycling C.

Annual production is about 50-70GT C yr\(^{-1}\), of which 0.1-0.2% is buried.

Several factors affect C preservation:
- organic matter production
- oxygen
- organic matter composition

It is difficult to isolate these factors from one another to elucidate underlying mechanisms