

Organic Matter Preservation in Marine Sediments

The Basics: preservation vs. degradation
-Hedges and Keil, 1995

Role of mineralogy in OM preservation
-Ransom et al., 1998

Selectivity of OM preservation
Hedges et al., 2001

What gets in preserved buried OM?
-Tegelaar et al., 1989
-Hwang and Druffel, 2003

Who Cares?

- Atmospheric oxygen: given the current rate of OM burial, oxygen in the atmosphere could be replaced in ~3 million years. Yet we assume that oxygen in the atmosphere has remained near present values (0.23 atm) for at least the past 500 million years. What keeps the system in whack?
- Patriotism (Oil): Where do fossil fuel source rocks come from and what controls their abundance/distribution.
- Climate change: how does carbon burial affect CO₂ sequestration from the atmosphere? What is the anthropogenic impact on carbon burial?

Hedges and Keil, 1995

Image of sub-monolayer, monolayer, super-monolayer
zones removed due to copyright restrictions.

The central conundrum

“The central conundrum of the global carbon and oxygen cycles is that extremely recalcitrant organic substances such as kerogen, soil humus, and riverine organic matter are extensively oxidized back to CO₂ in relatively short time periods on land and in the ocean, whereas seemingly reactive remains of recently living marine organisms are preserved in depositing marine sediments. By what process might fossil material exhibiting the reactivity of plastic encased in brick be extensively respired and how is such severe mineralization turned off at the ocean floor and along continental margins?”

How does reactivity of OM fractions affect preservation?

Preservation is the opposite of degradation!

Graph of O₂ effect removed due to copyright restrictions.

The most slowly degrading component has the greatest impact in highly degraded environments

The Missing Link...Sedimentation rate, oxygen...what really matters?

Sediment accumulation rate:

- OC accumulation rate vs bulk sedimentation rate: properties are not independent!
- %OC is affected by “dilution” from coarse organic poor sediment fraction

-- **Burial efficiency** is a more useful measure --

Bottom water dissolved oxygen:

- Dynamic comparisons of mineralization rates in oxic vs. anoxic environments shows no evidence for an “oxygen effect” (with the exception of hydrolysis-resistant compounds)
- Concentration-based evidence of bottom water oxygen show no *universal* correlation in marine sediments (to be continued...)

-- **Oxygen exposure time** is more meaningful --

But there's still hope!

- Sediment surface area appears to have strong correlation to %OC, suggesting **sorption** as a mechanism for preservation.

Figure 4: (Carpenter et al., 1981, 1982) Graph of plot of weight percent of organic carbon (%OC) vs. accumulation rate for sediments from a variety of dispositional environments removed due to copyright restrictions.

Figure 5: data compiled from Hendrichs, 1992, 1993) Graph of plot of percent burial efficiency of sedimentary organic carbon vs. sediment accumulation rate at different sites removed due to copyright restrictions.

Figure 6: (after Betts and Holland, 1991) Graph of plot of percent burial efficiency vs. the corresponding bottom water oxygen concentration at different dispositional sites removed due to copyright restrictions.

Figure 7: (data from Keil et al., 1994a) Graph of weight percent of organic carbon plotted vs. mineral surface area removed due to copyright restrictions.

Sorptive preservation and the mysterious monolayer equivalent

- Observations suggest a roughly “monolayer equivalent” coating in continental shelf/slope environments, with submonolayer coatings occurring in deltaic sediments and the open ocean, and greater-than-monolayer occurring in high productivity regions.
- Mineral surface areas higher than predicted for smooth surface model, suggesting rough mineral surfaces (possibly providing protective pores)
- Sorption suggests that organic matter was dissolved at one time.
- Reversible sorption (~80%) is indicated by experimental evidence. This would imply a dynamic relationship between sedimentary POM, DOM, and mineral surfaces, with DOM acting as a “*buffer*” for labile POM.

The Oxygen Effect

Figure depicting the Oxygen Effect removed due to copyright restrictions.

A Transition Zone ?

- Authors propose a transition from sorptive protection in continental shelf/upper slope sediments to oxic degradation in lower slope/deep sea sediments
- The idea is that faster sedimentation rates result in shorter oxygen exposure times at continental locations
- But why would OM be more susceptible to slow oxic degradation than aneorobic degradation?
 - Non-hydrolyzable compounds that are resistant to fermentative degradation.
 - Some compounds may only be degraded by enzymes requiring molecular oxygen (oxygenases, dyhydrogenases)
 - Production of reactive species (radicals, peroxide)

Graphs of %OC vs. depth, pollen, and pollen slit vs. time of exposure removed due to copyright restrictions.

And finally...

Proposed Feedbacks controlling OM burial

- Surface Area conservation of continental weathering products
- OC/S ratio controlled by reactive Fe/surface area.

And the million dollar question is...

- Why does sorbed OM resist degradation but succumb to slow oxic degradation?

Ransom et al., 1998

Does size matter (for surface area)?

- Surface roughness does not account for the discrepancies between measured surface areas and surface areas predicted for a smooth geometrical object.
- High measured surface area could be caused by inadvertent inclusion of fine (SA $\sim 100 \text{ m}^2/\text{g}$) particles with coarse fraction (SA $\sim 0.001 - 1 \text{ m}^2/\text{g}$)
- A small wt% of fine particles can generate significant increase in surface area

Graphs of surface area vs. pit depth and total sample surface area vs. high surface area material removed due to copyright restrictions.

Surface area or *minerology*?

Graphs of Smecite vs. grain size removed due to copyright restrictions.

Graphs of TOC vs. specific surface area and clay + opal removed due to copyright restrictions

Carbon loading depends on mineral type

Graph of correlation of TOC and specific surface area for sediments removed due to copyright restrictions.

- Poor correlation between surface area and TOC at SLO and NM sites.
- Strong relationship between *clay fraction* surface area and TOC.
- Sites differ in the relative abundance of smectite and chlorite (Fig 7a)
- Differences in the slope (Fig 7b) of TOC vs. clay fraction SA possibly linked to differences in flocculation, surface chemistry, or density of available sites for sorption for different types of clays.

Graphs of weight percent smectite vs. chlorite in the clay fraction of sediments removed due to copyright restrictions.

Hedges et al., 2001

Figure 1 removed due to copyright restrictions.

- No significant (detectable) compositional change in POM through the water column...even though >98% of surface OM is degraded at depth
- No evidence for selective enrichment of aliphatic algeenan or increase in unsaturated C, which would be indicative of humification
- Data is supported by constant C/N
- Proposed physical protection by mineral or refractory organic matrix

Figure 2 removed due to copyright restrictions.

E. W. Tegelaar et al.: Thoughts on kerogen formation.

Figure of proposed mechanism for kerogen formation describing the interrelationships between extant biomass, kerogen and fossil fuels removed due to copyright restrictions.

- Kerogen formation by selective preservation of resistant biomacromolecules
- Microscopical observations of biological “structures” in kerogen

Hwang and Druffel, 2003: Is uncharacterized OM made of lipids?

Graph of organic fraction (%) vs. $\Delta^{14}\text{C}$ bulk POC removed due to copyright restrictions

Graph of $\Delta^{14}\text{C}$ vs. $\Delta^{14}\text{C}$ bulk POC removed due to copyright restrictions.

Why is the lipid fraction so depleted with respect to carbon-13?

Graph of $\delta^{13}\text{C}$ vs. $\delta^{13}\text{C}$ bulk POC removed due to copyright restrictions.

Conclusions

- Buried carbon is marine in origin.
- Association with mineral surfaces may protect organic matter from degradation
- Mineralogy affects organic matter loading
- Slow oxic degradation is important in the deep ocean
- NMR evidence suggests non-selective preservation of POC in the water column
- Isotopic evidence suggests lipid as major component of uncharacterized OM in POC

Questions to ponder

- So, is it physical protection (ie. mineral surface) or selective preservation of refractory compounds that controls the amount and composition of organic matter burial?
- What are the fundamental differences in mechanisms of degradation and preservation in the water column and in sediments?
- Is OM burial at steady state? On what time scales?
- In the geologic record, did organic carbon burial begin as a result of the emergence of degradation-resistant biomolecules or was it simply a response to increasing global OM production mediated by non-selective processes?