#### What are the mechanisms of C preservation?

Primary production: The higher PP, the higher the flux of OM, the more rapidly the C/N/P transits the "reactive" zone of active C degradation.

Oxygen: Anaerobic systems require microbial consortia to degrade OM that are inherently less efficient than aerobic organisms. Low oxygen limits the presence of aerobic respiration thereby preserving C. Longer initial preservation, or other factors (presence of S-) may lead to more extensive "geopolymerization" that more permanently preserves C.

There are intrinsically labile and non-labile structures of biomolecules. The mix of these will affect the amount of C preserved.

If you want to understand why C is preserved in marine sediments, look at where it is buried....



Fig. 1. Idealized diagram depicting current estimates of the percentage of total organic matter burial occurring within various marine sediment types (see Table 2). Light sections represent sediments which contain organic loadings lowe yr than a monolayer equivalent. Stippled sediments contain monolayer-equivalent loadings, and dark sediments contain loadings that are more than monolayer-equivalent.

#### Tabulation of C burial in marine sediments

#### Table 2 Organic carbon burial rates (and percentages) in different ocean regimes

Sediment type	Deltaic	Shelf	Slope	Pelagic	Total
Data from Gershanovich et al. (1974)					
All sediment types	0(0)	23 (10)	195 (88)	5 (2)	223
					$\Sigma = 223$
Data from Berner (1989)					
Terrigenous deltaic-shelf sediments	104 (82)	0	0	0	104
Biogenous sediments (high-productivity zones)	9	0	7 (6)	3 (2)	10
Shallow-water carbonates	0	6 (5)	0	0	6
Pelagic sediments (low-productivity zones)	0	0	0	5 (4)	5
Anoxic basins (e.g. Black Sea)	0	1(1)	0	0	1
					$\Sigma = 126$
Recalculation of data from Berner (1989) *					
Deltaic sediments	70 (44)	0	0	0	70
Shelves and upper slopes	0	68 (42)			68
Biogenous sediments (high-productivity zones)	0	0	7 (4)	3 (2)	10
Shallow-water carbonates	0	6 (4)	0	0	6
Pelagic sediments (low-productivity zones)	0	0	0	5 (3)	5
Anoxic basins (e.g. Black Sea)	0	1 (0.5)	0	0	1
					$\Sigma = 160$

Units are 1012 g C yr<sup>-1</sup> (parenthetical units = % of total burial).

<sup>a</sup> Deltaic-shelf sediments were reapportioned assuming that 33% of the sediment discharge from rivers is deposited either along non-delatic shelves or upper slopes, and assuming that those deposits have total loadings of 1.5% organic carbon rather than 0.7% as in delatic regions. Estimates for all other regions remain the same.

#### Protection and preservation of C on mineral surfaces

Larry Mayer and others reasoned that there is no such thing as a naked mineral surface in seawater. Further, the amount of C that can be loaded onto a sediment particle is proportional to its surface area.



### Organic carbon vs surface area for sediments from the Gulf of Maine



# Organic carbon vs surface area for sediments from the Gulf of Maine



# Organic carbon vs surface area for sediments from the Gulf of Maine



Surfaces are coated with organic matter to the equivalent of one molecule thick...

#### Organic carbon, mineral surface area, and depth in Gulf of Maine Sediments



Sediments may be overloaded with C due to biogeochemical cycling, but eventually diagenesis will reduce the C load to a set surface area vs %OC value

Mineral surface area vs %organic carbon for Columbia River Sediments (Hedges and Keil, Mar. Chem (1995) 49, 81-115.)



# Surface area vs %organic carbon for sediments from low oxygen depositional regimes



Surface area vs % organic carbon for Equatorial Pacific sediments



Surface area vs % organic carbon for deltaic and river sediments



Proposed mechanism for surface protection adsorption of organic matter into very small pores



### Distribution of mineral pore sizes in marine sediments



### Distribution of mineral pore sizes in marine sediments



#### Surface area control on OC preservation in marine sediment..

Weathering introduces new mineral surfaces constantly to the environment.

These surfaces ultimately become coated with organic matter, at approximately a monolayer equivalent loading.

Under conditions that are typical for sediment deposition on continental margins (where most C is buried) degradation proceeds to the ME loading and slows sufficiently there after to preserve this amount of carbon.

In open ocean setting, where oxygen exposure times are much longer, degradation proceeds to < ME loadings. In anoxic basins, where oxygen exposure times are much shorter, loadings are > ME.

Mechanism is preservation in small pores that are inaccessible to enzymes. e.g. *physical protection*. What is the problem with this model???

Hint.....think of the  $\delta^{13}$ C of marine sediments.



#### The rebuttal to surface area control on OC preservation.....

Theoretical surface area of a 1 mm pitted spherical particle



It is impossible to physically protect that much organic matter in pits & cracks

### Effect of high surface area material on total surface area



Mineral surface area vs %organic carbon for Columbia River Sediments (Hedges and Keil, Mar. Chem (1995) 49, 81-115.)



#### Surface area vs %TOC in Washington margin sediments (Keil et al, (1994) GCA, 58, 879-893.



### Grain size, smectite, opal, and surface area in Washington margin sediments



#### Correlation of surface area, TOC, Clay minerals+opal in Washington margin sediments



#### TOC vs surface are for California margin sediments



## Correlation of clay minerals with TOC in coastal sediments

Ransom et al., GCA (1998) 62, 1329-1345



surface area, clay fraction (m<sup>2</sup> g<sup>-1</sup>)

### Correlation of clay minerals with TOC in coastal sediments



### Clay mineralogy, not simple surface area drives OC preservation



.....and finally the mechanism of preservation....

Mayer-Hedges-Keil hypothesis





Physical protection from enzymatic degradation in small pores/cracks



No physical protection OM is on surface and only a small fraction is in contact with mineral. Things to remember.....

Most OM is preserved in continental margin sediments

Carbon loading is proportional to surface area

Sedimentation rate, or rate of burial may be a factor

Effect of oxygen is open, some evoke it, some do not. not clear if or how it is a factor.

Mechanism of C preservation is also open. Physical protection has been argued, but how this works may not be understood.