

## 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....

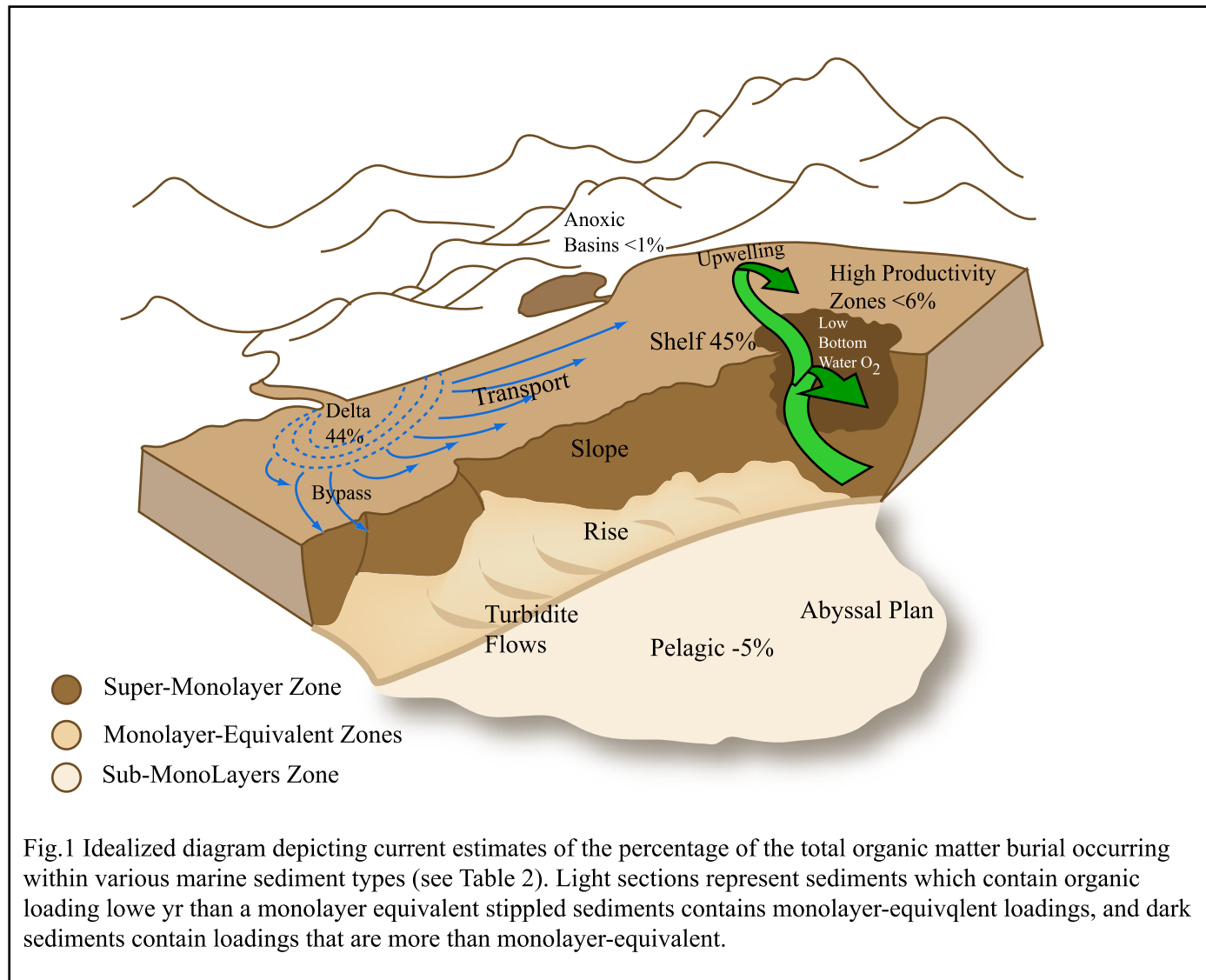


Figure by MIT OCW.

# Tabulation of C burial in marine sediments

## Organic Carbon Burial Rates (and percentages) in Different Ocean Regimes

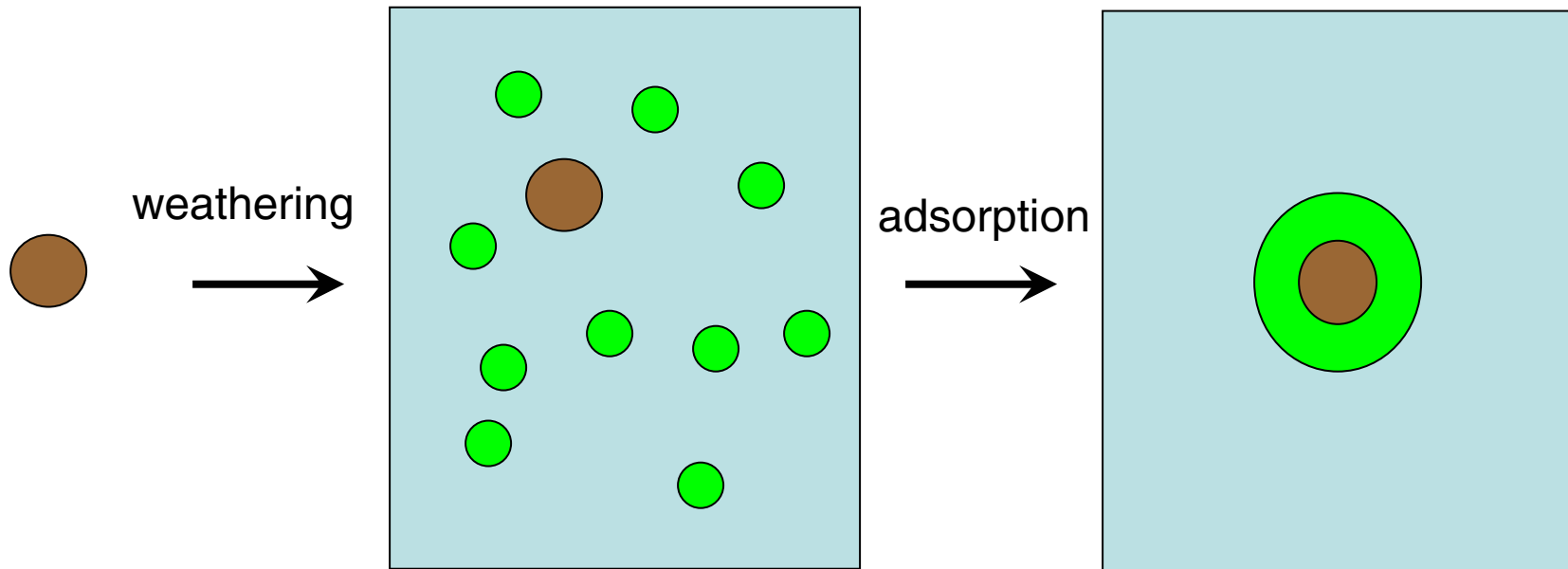
Sediment type	Deltaic	Shelf	Slope	Pelagic	Total
<b>Data from Gershanovich et al. (1974)</b>					
All sediment types	0 (0)	23 (10)	195 (88)	5 (2)	223 e = 223
<b>Data from Berner (1989)</b>					
Terrigenous deltaic-shelf sediments	104 (82)	0	0	0	104
Biogenous sediments (high-productivity zones)	0	0	7 (6)	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
					$\Sigma = 126$
<b>Recalculation of data from Berner (1989)</b>					
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 10<sup>12</sup> gCyr<sup>-1</sup> (parenthetical units = percent of total burial).

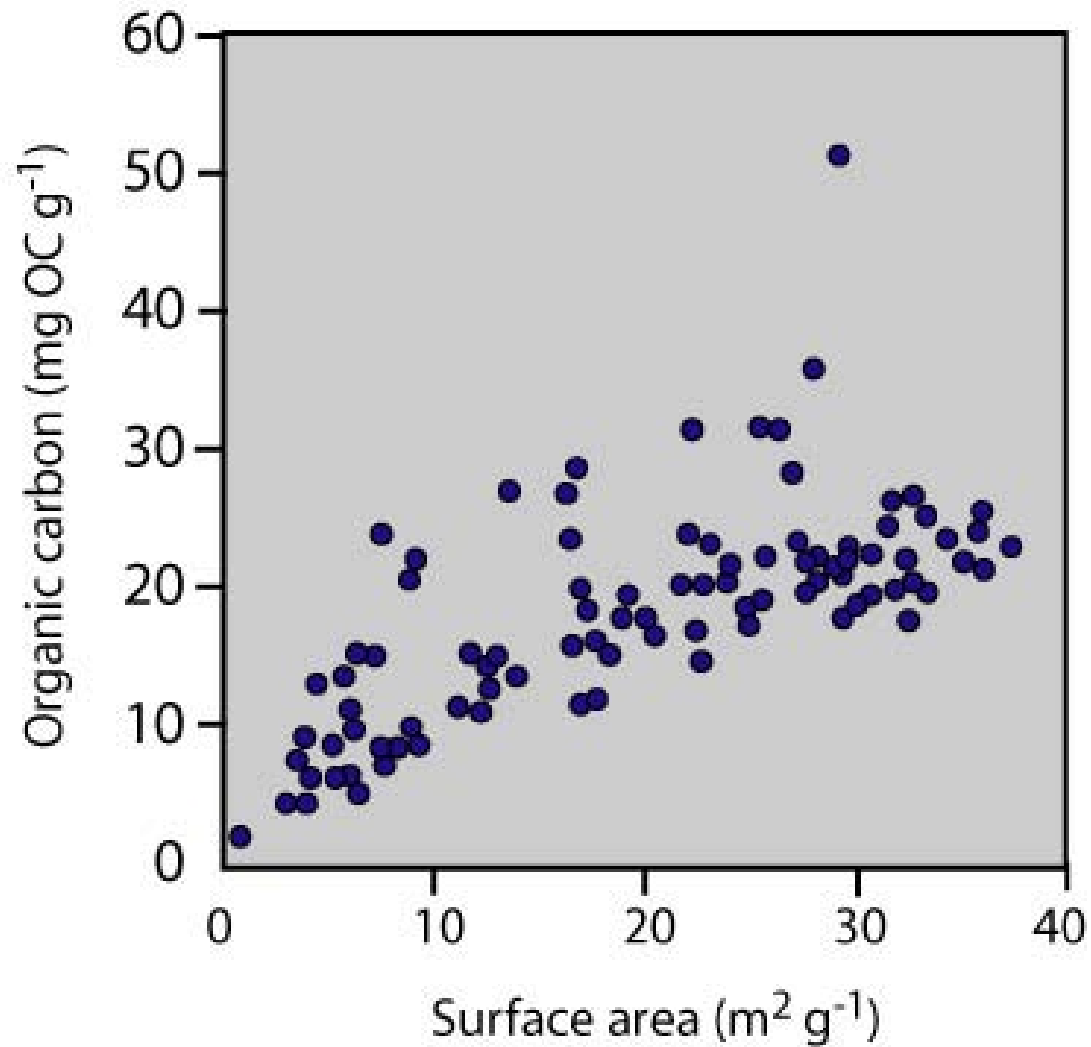
\*Deltaic-shelf sediments were reapportioned assuming that 33% of the sediment discharge from rivers is deposited either along non-deltaic shelves or upper slopes, and assuming that those deposits have total loadings of 1.5% organic carbon rather than 0.7% as in deltaic regions. Estimate for all other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

# Protection and preservation of C on mineral surfaces

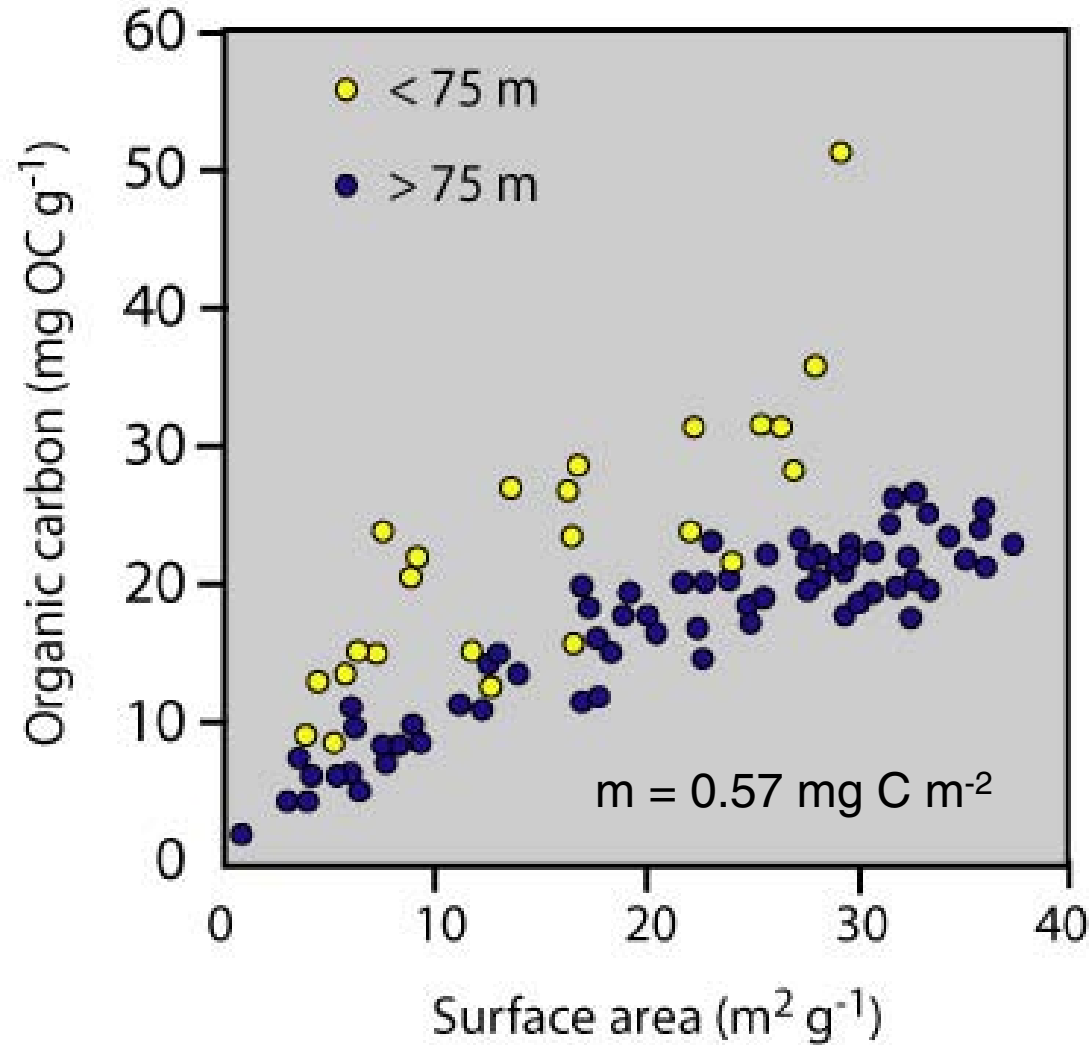
Larry Mayer and others reasoned that there is no such thing as a naked mineral surface in seawater. Further, the amount of C that can be loaded onto a sediment particle is proportional to its surface area.



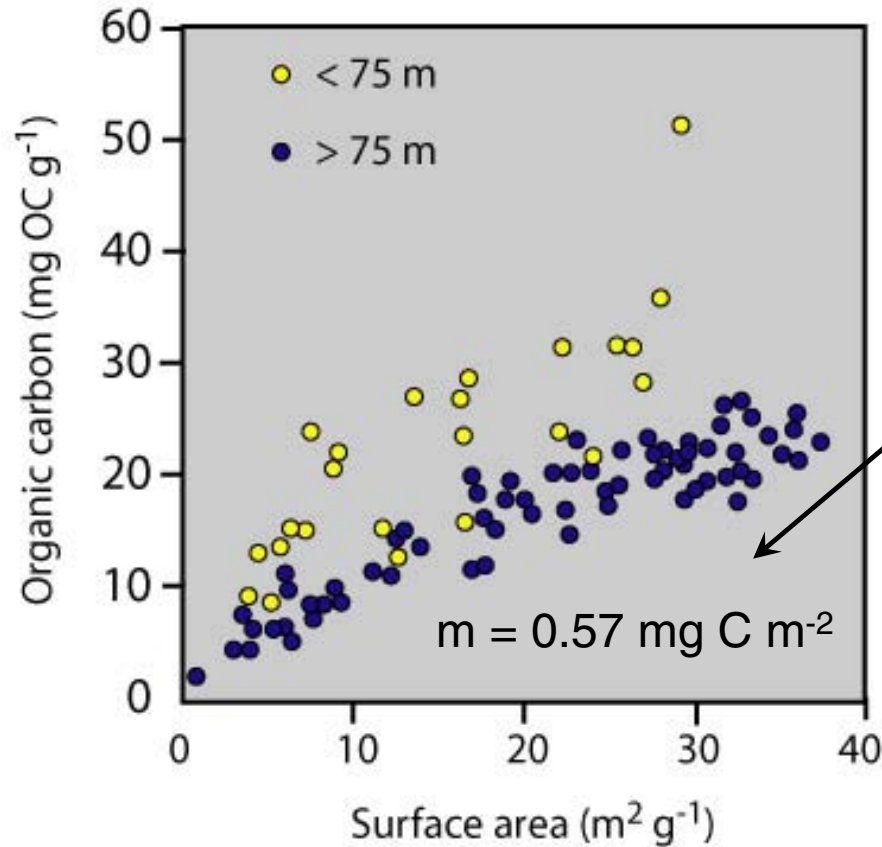
# Organic carbon vs surface area for sediments from the Gulf of Maine



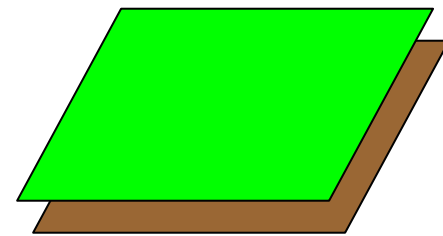
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# Organic carbon vs surface area for sediments from the Gulf of Maine

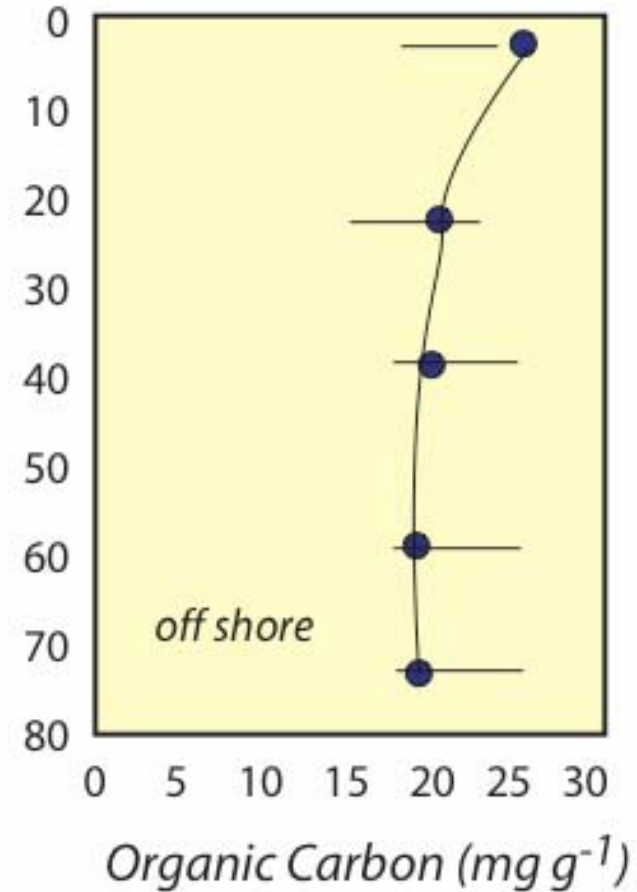
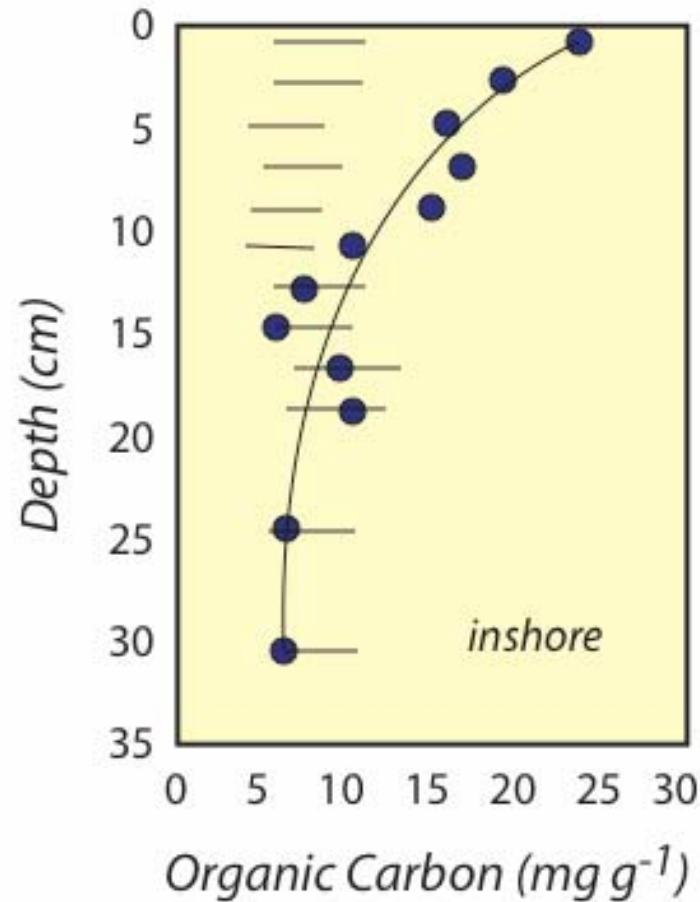


Monolayer equivalent (ME) loading



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

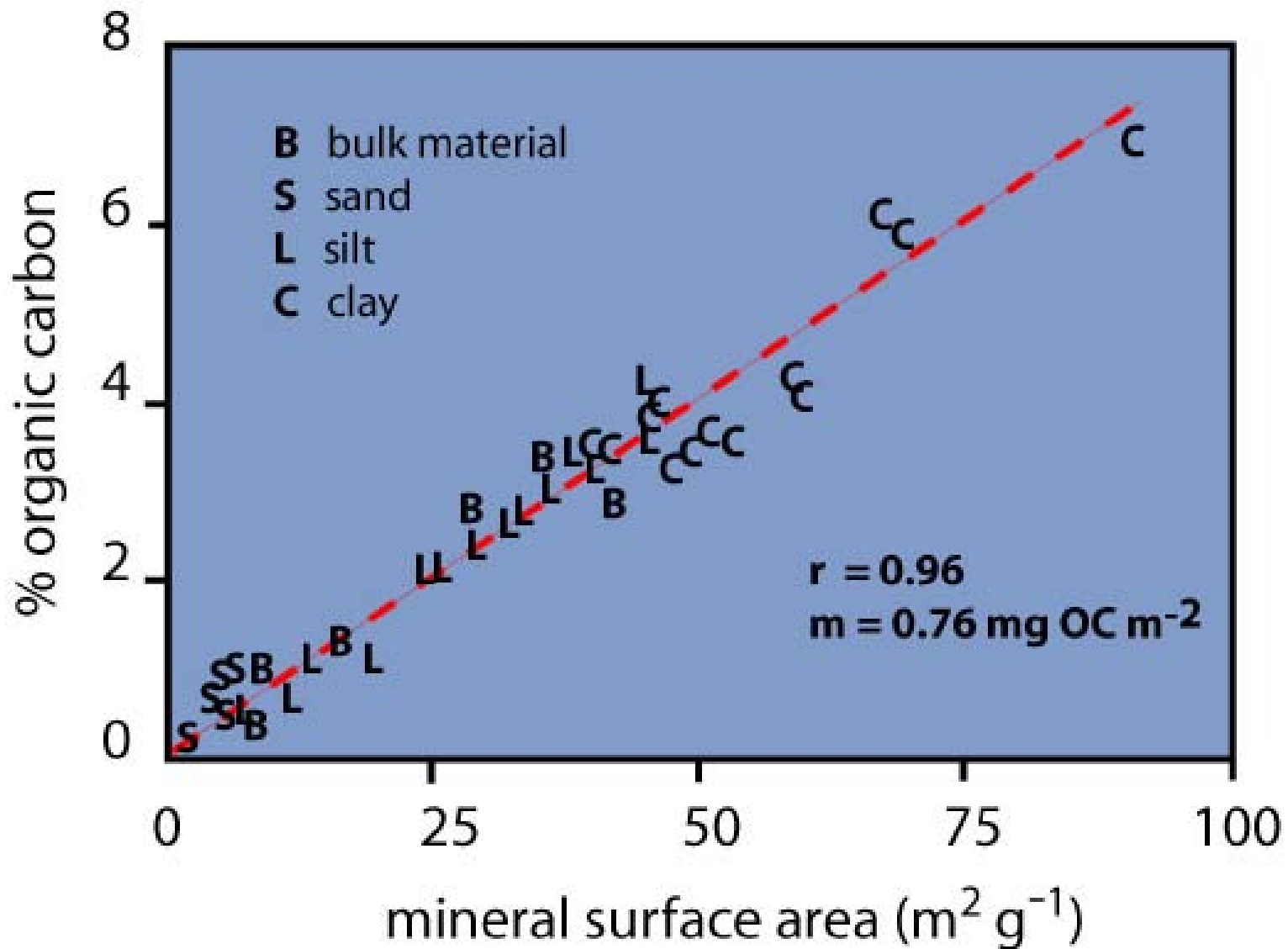
*Organic carbon, mineral surface area, and depth  
in Gulf of Maine Sediments*



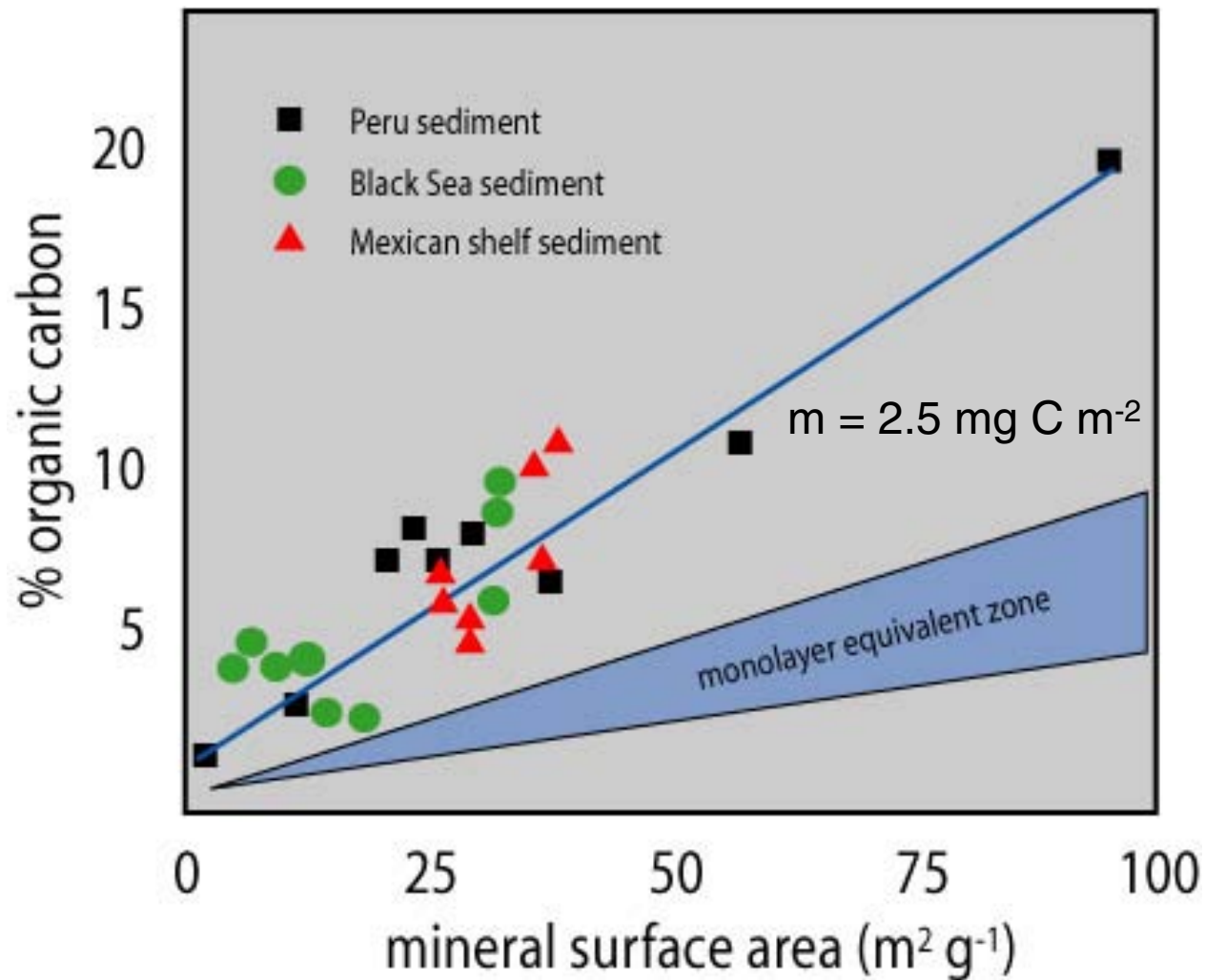
Sediments may be overloaded with C due to biogeochemical cycling, but eventually diagenesis will reduce the C load to a set surface area vs %OC value



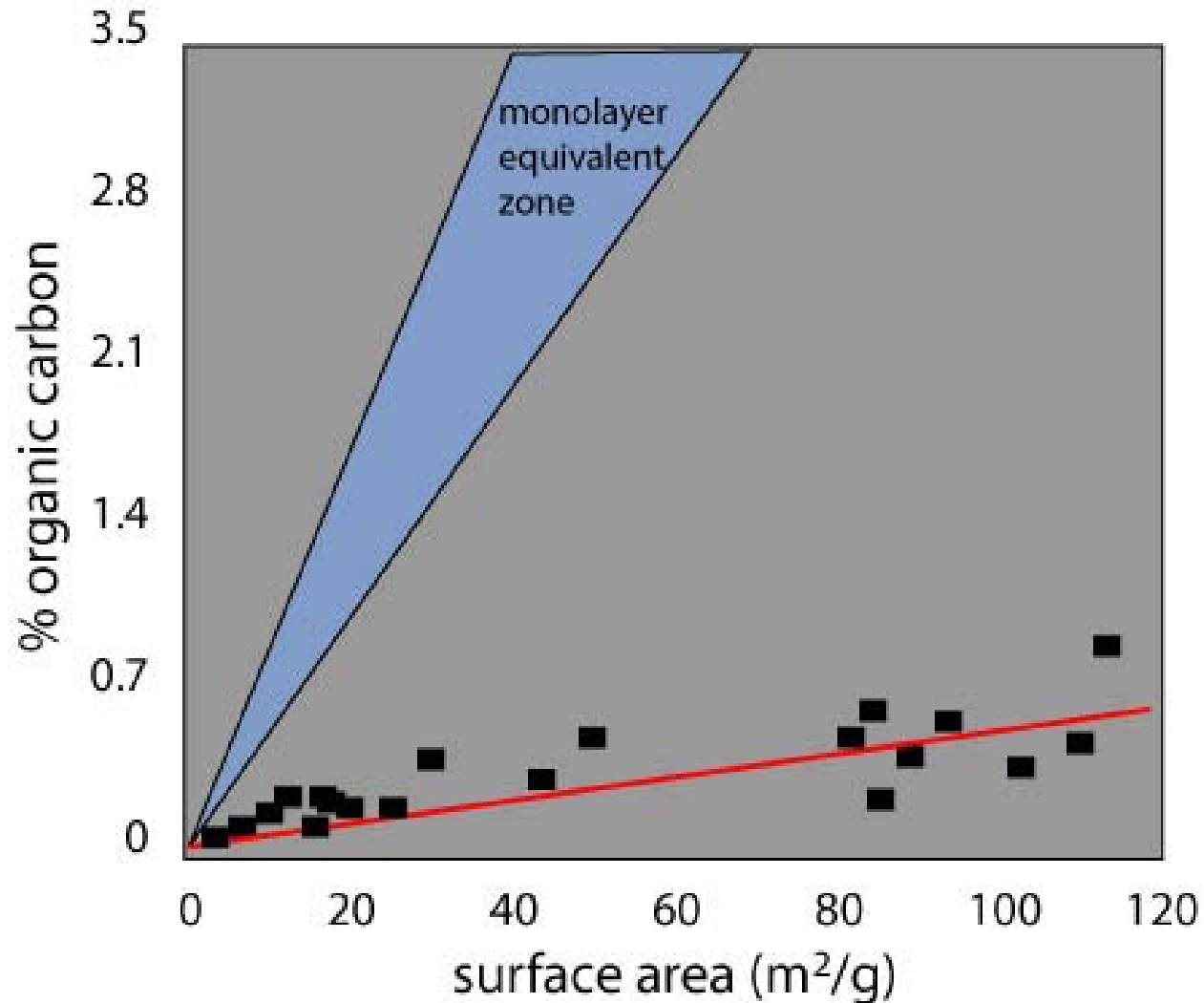
Mineral surface area vs %organic carbon for Columbia River Sediments  
(Hedges and Keil, Mar. Chem (1995) 49, 81-115.)



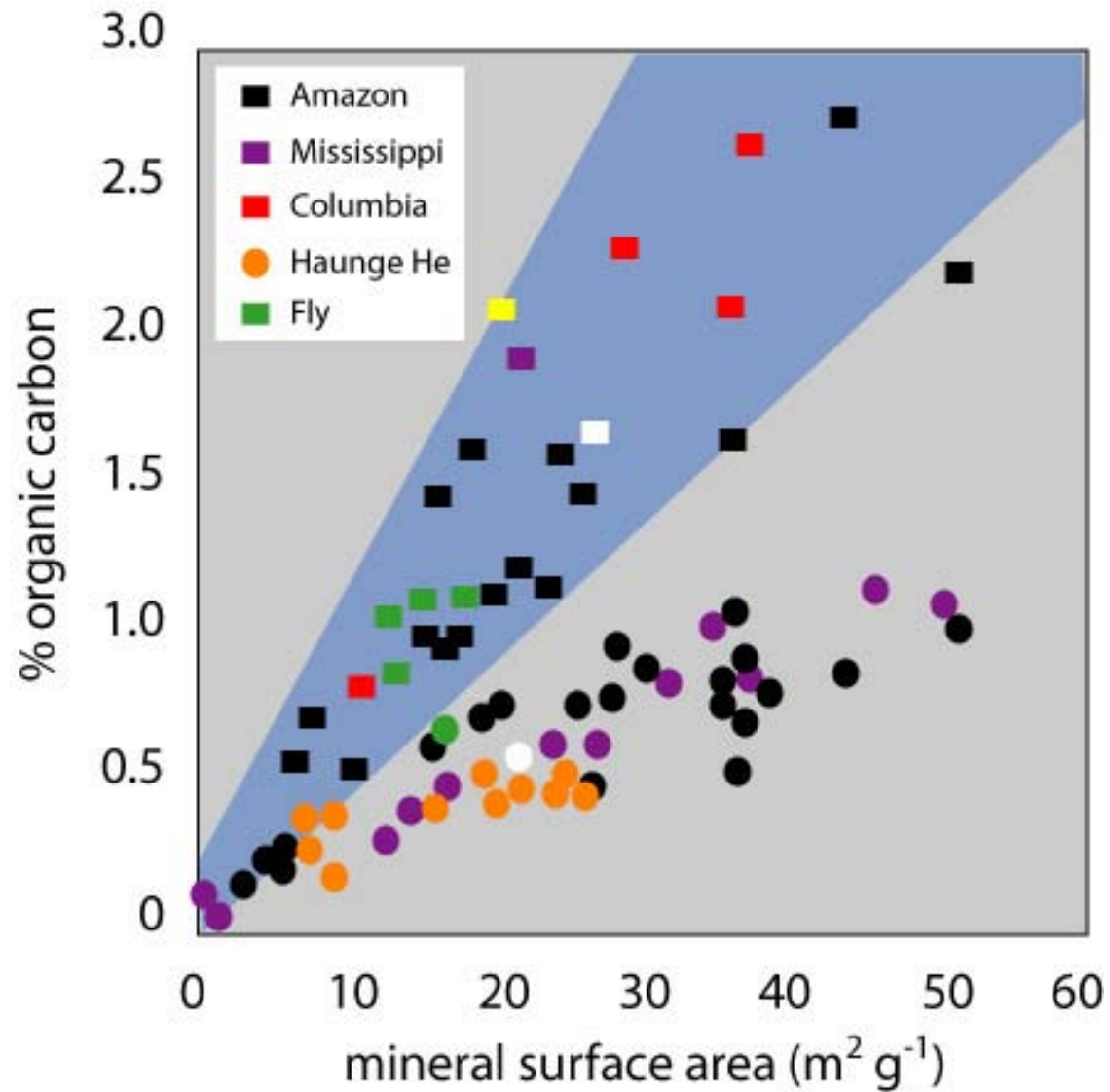
# Surface area vs %organic carbon for sediments from low oxygen depositional regimes



## Surface area vs % organic carbon for Equatorial Pacific sediments

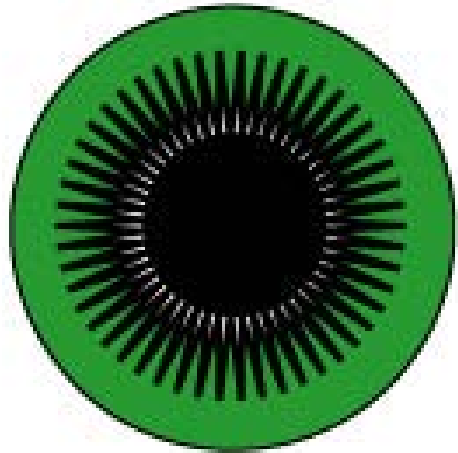


## Surface area vs % organic carbon for deltaic and river sediments



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

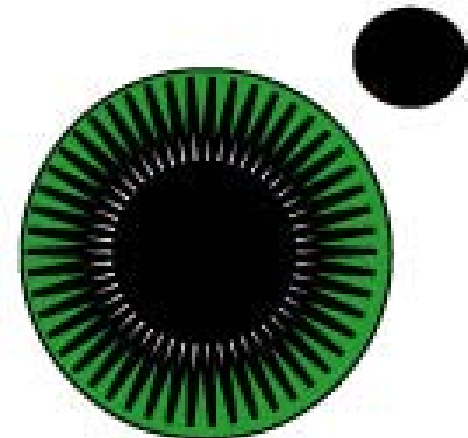
organic coated particle



degradation

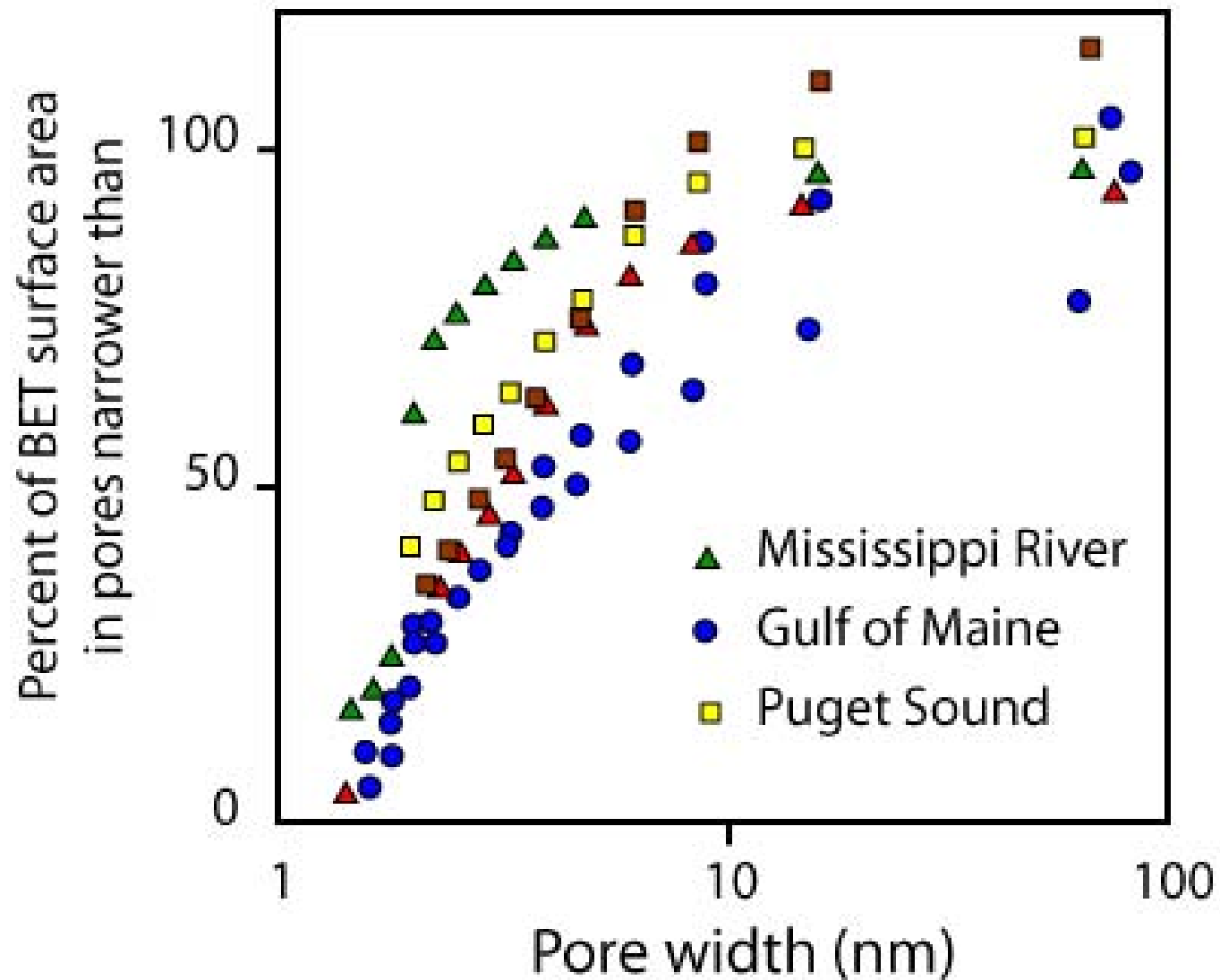


enzyme

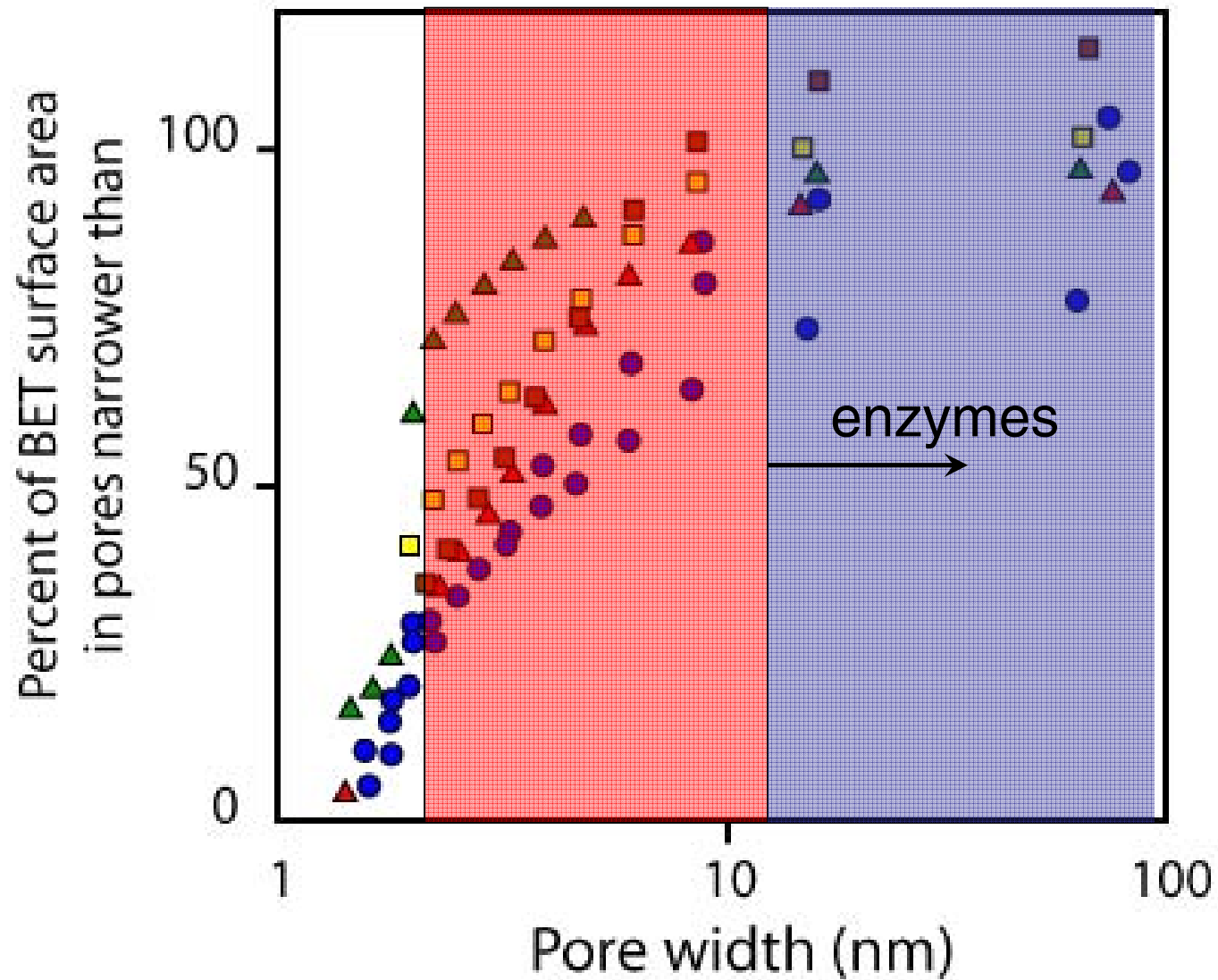


ME coating of  
organic matter

# 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.

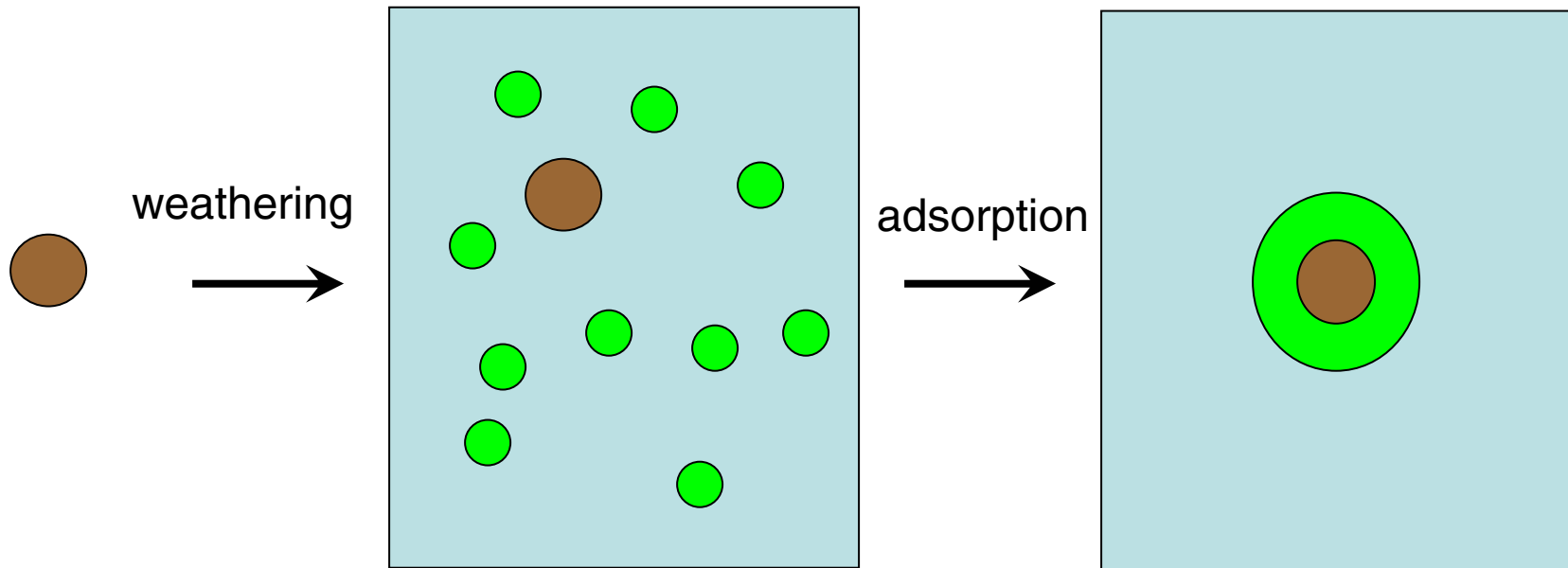
In open ocean setting, where oxygen exposure times are much longer, degradation proceeds to  $<$  ME loadings. In anoxic basins, where oxygen exposure times are much shorter, loadings are  $>$  ME.

Mechanism is preservation in small pores that are inaccessible to enzymes.  
e.g. ***physical protection***.



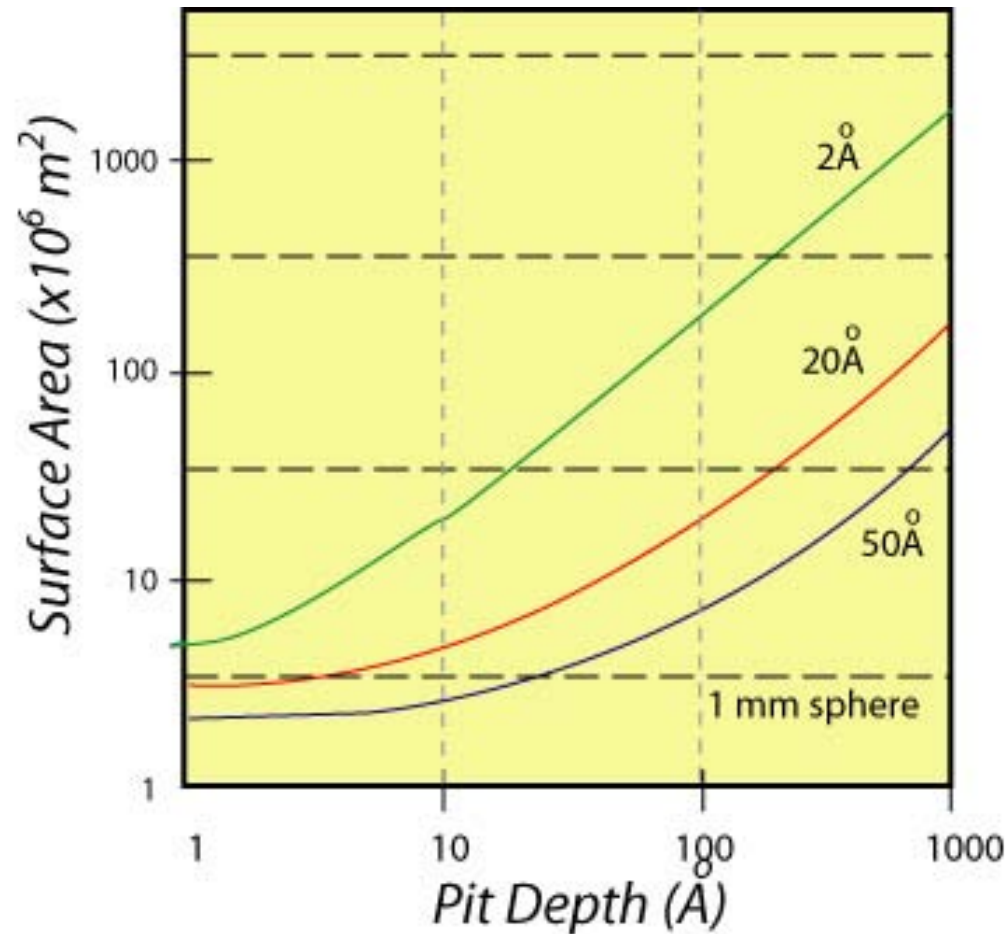
What is the problem with this model???

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



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

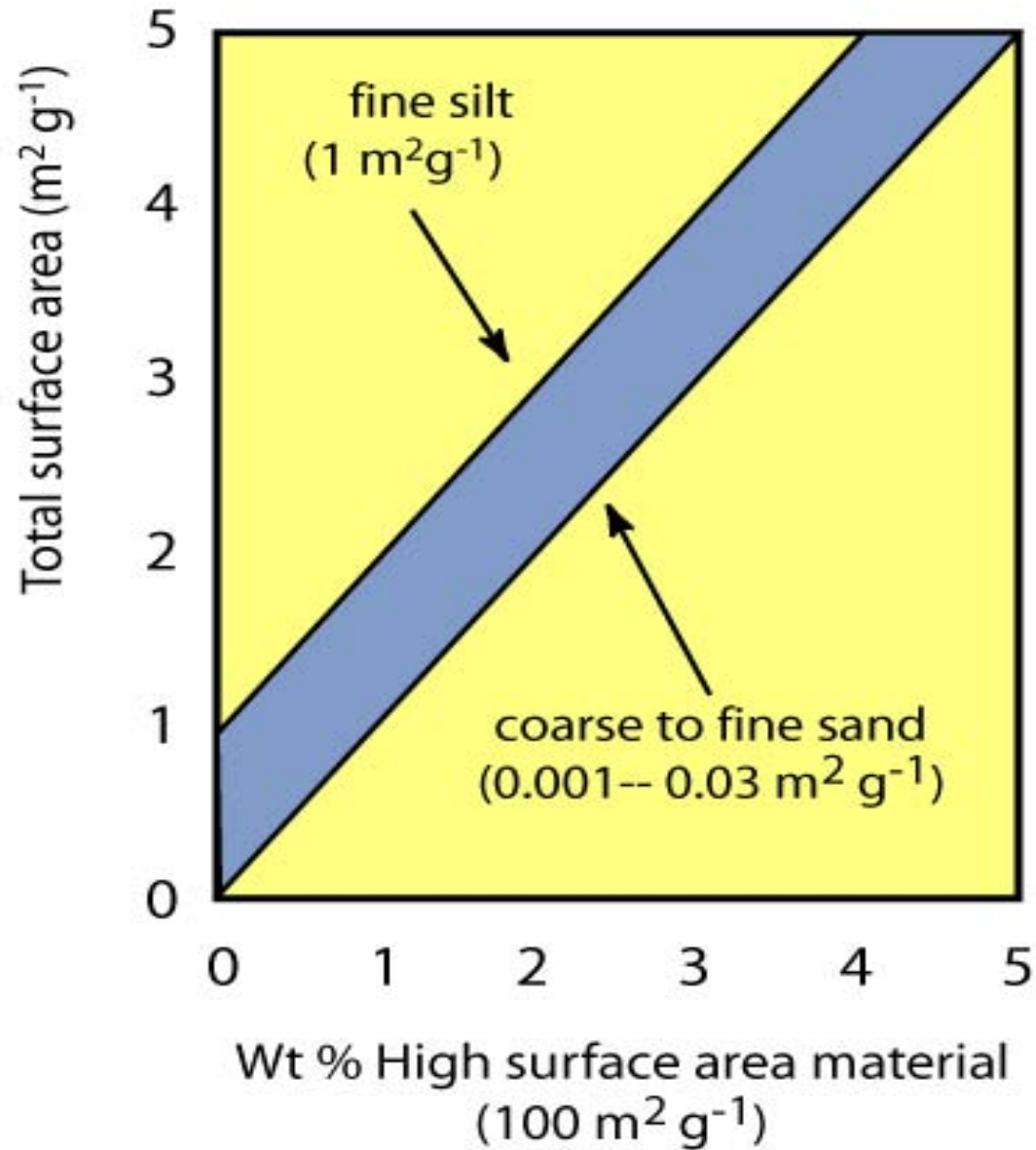
Theoretical surface area of a 1 mm pitted spherical particle



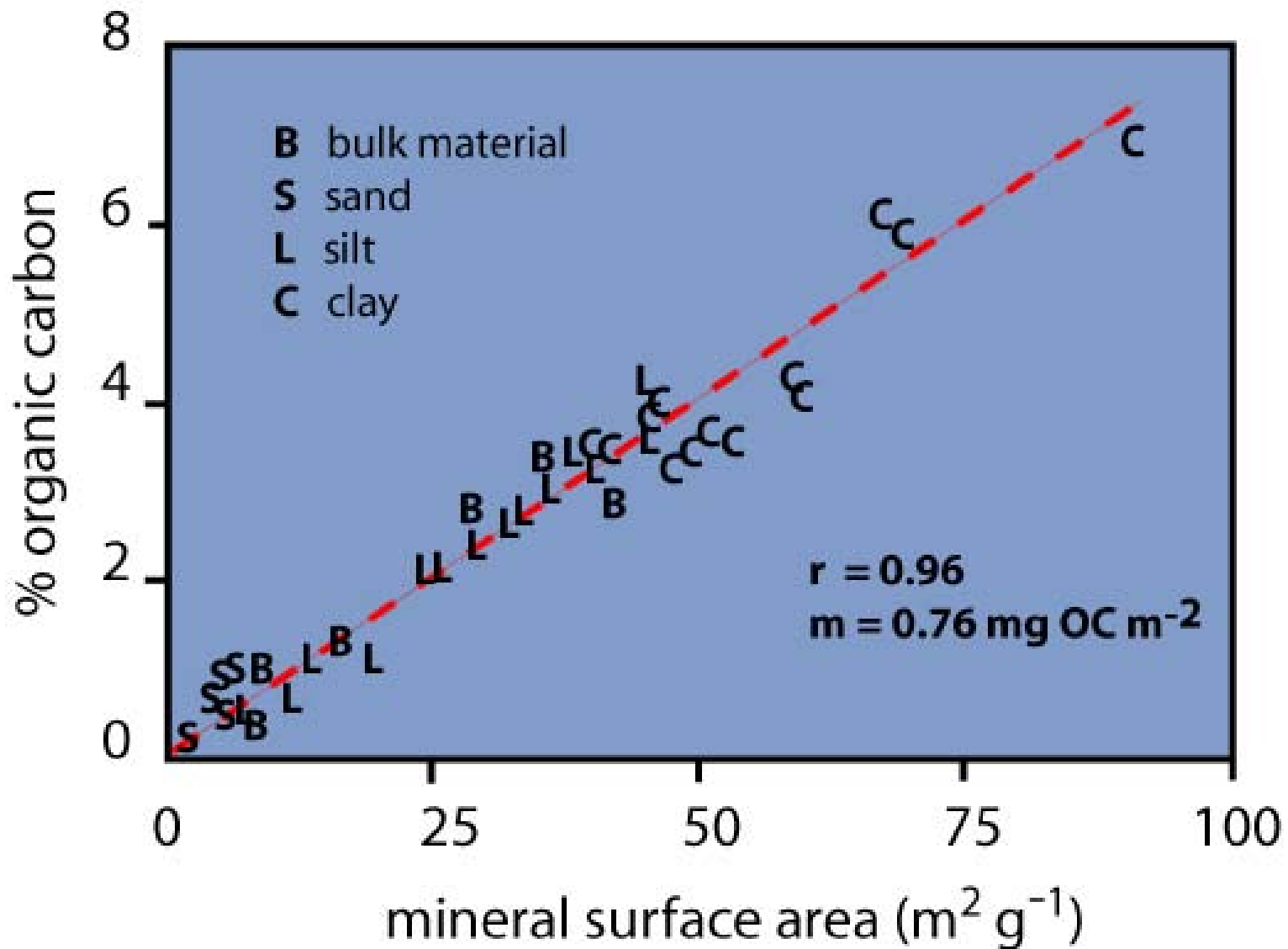
*It is impossible to physically protect that much organic matter in pits & cracks*

# Effect of high surface area material on total surface area

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

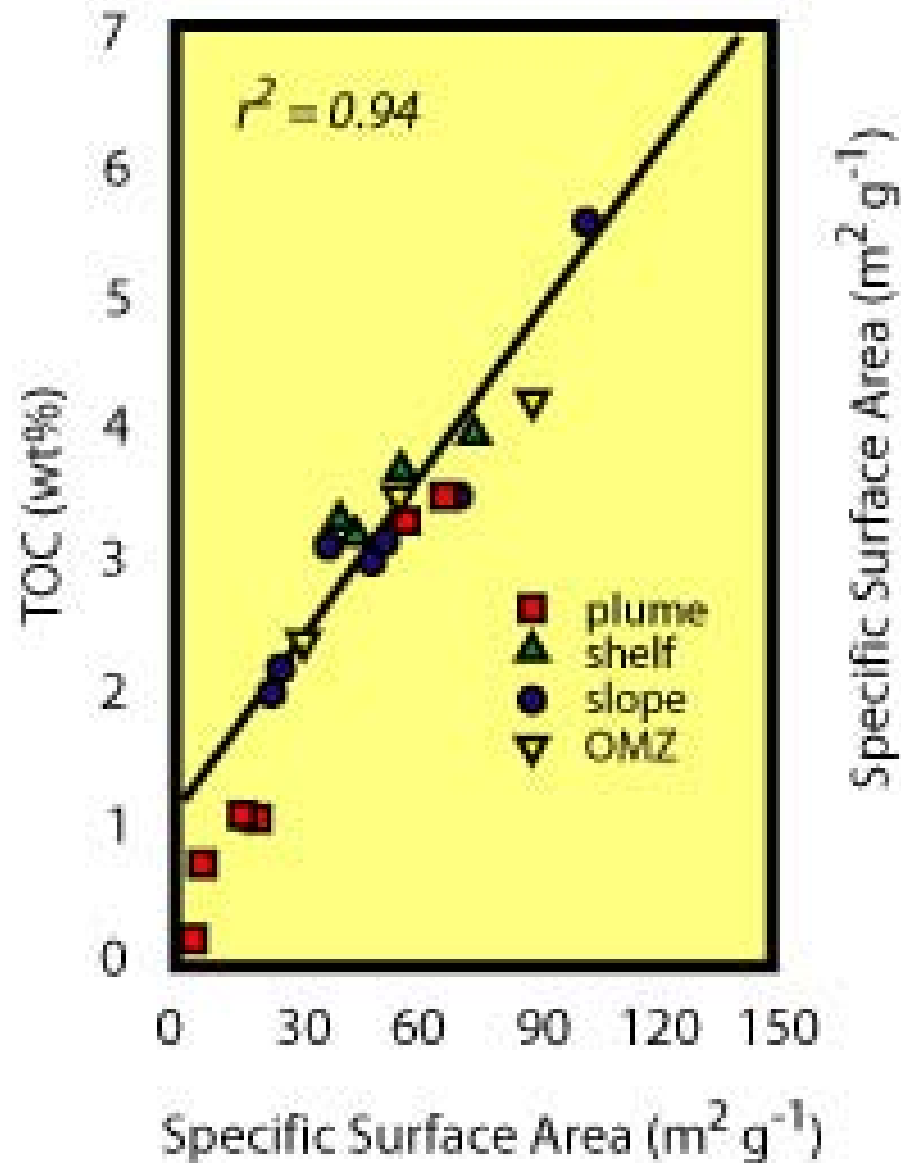


Mineral surface area vs %organic carbon for Columbia River Sediments  
(Hedges and Keil, Mar. Chem (1995) 49, 81-115.)

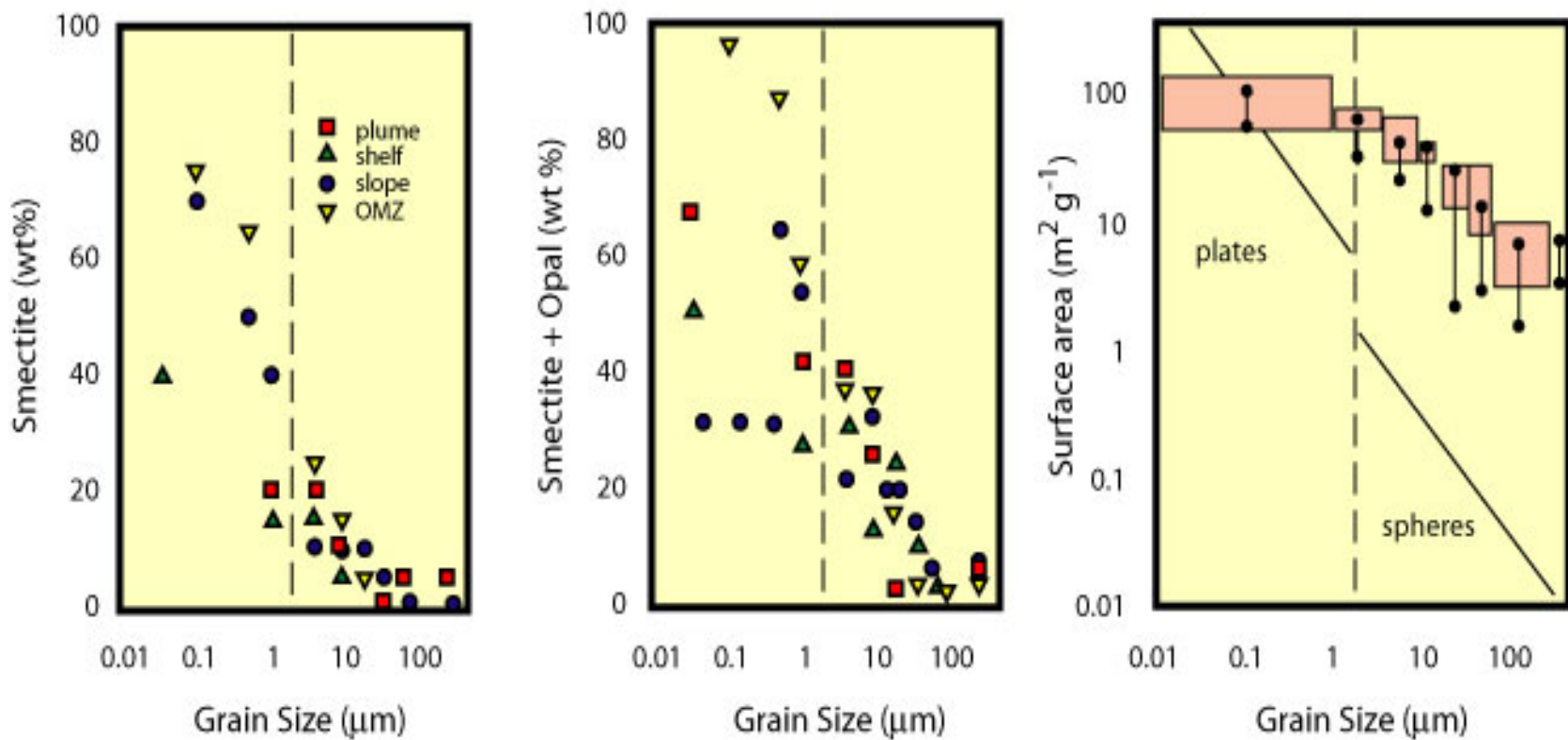


# Surface area vs %TOC in Washington margin sediments

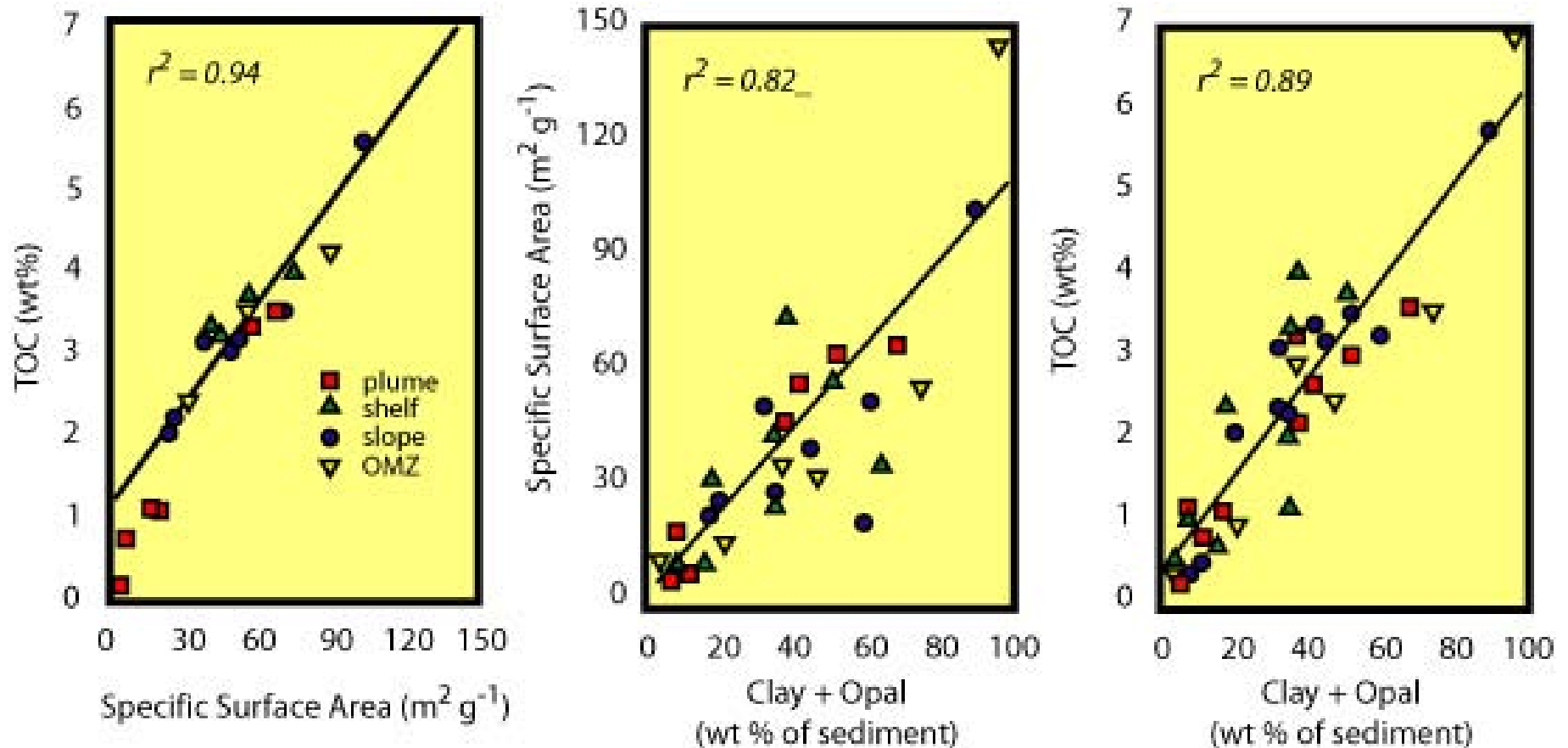
(Keil et al, (1994) GCA, 58, 879-893.



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

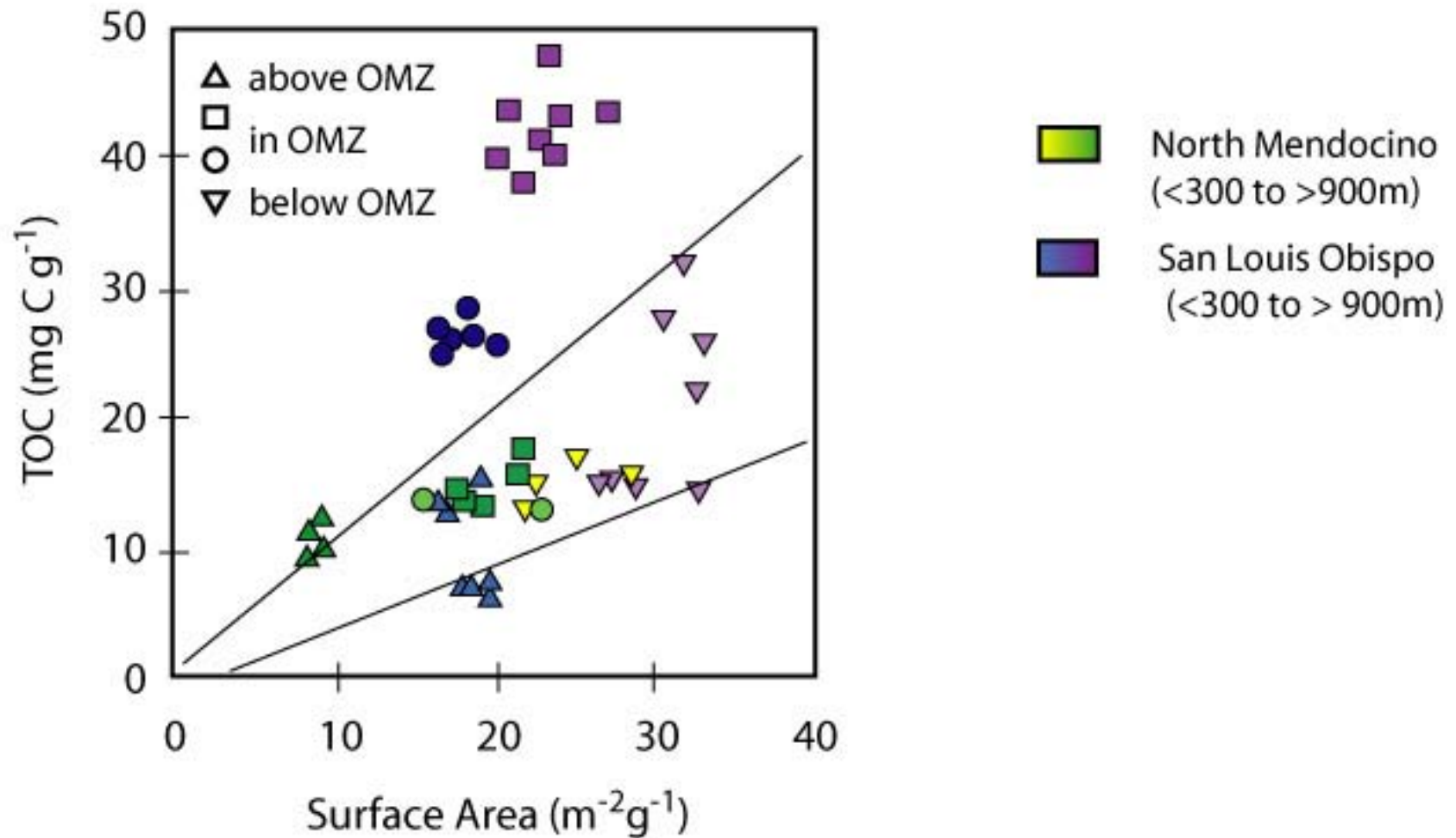


## Correlation of surface area, TOC, Clay minerals+opal in Washington margin sediments



# TOC vs surface area for California margin sediments

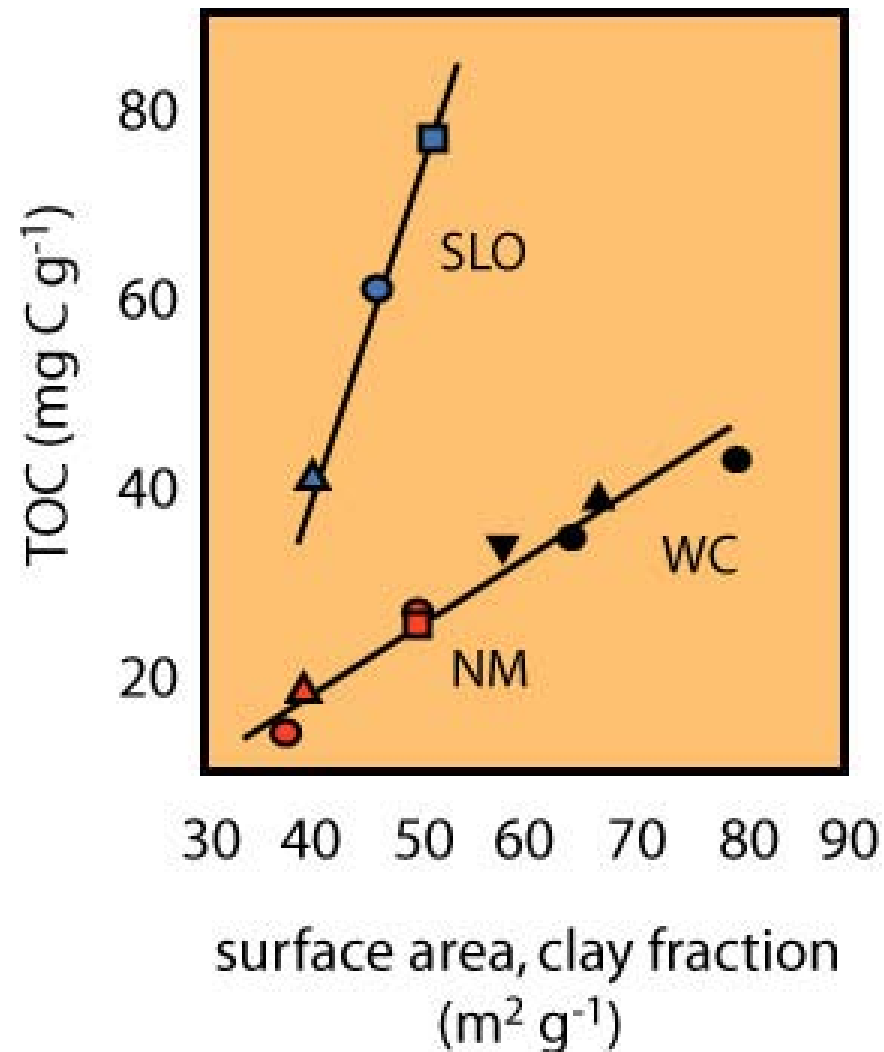
Ransom et al., GCA (1998) 62, 1329-1345





# Correlation of clay minerals with TOC in coastal sediments

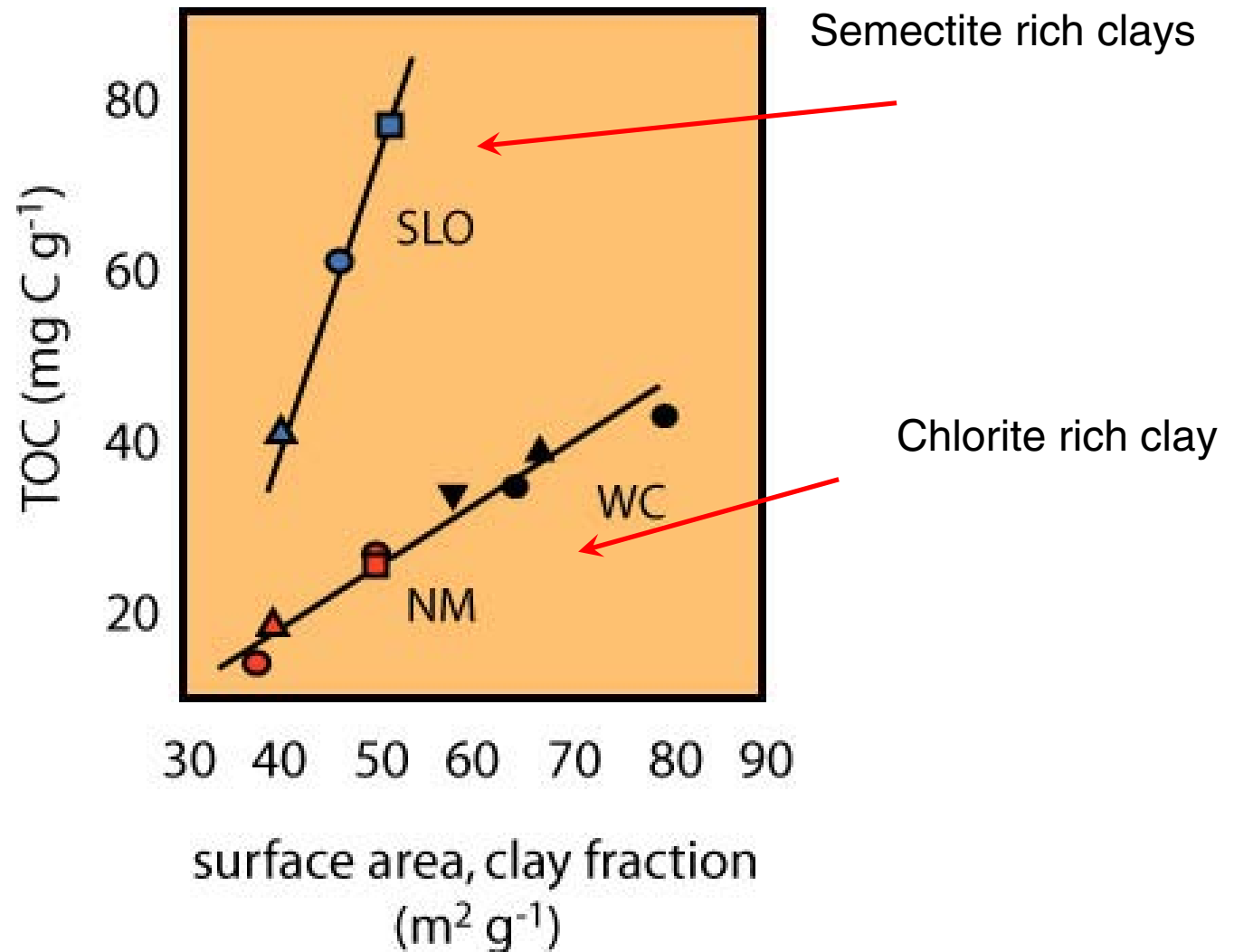
Ransom et al., GCA (1998) 62, 1329-1345



# Correlation of clay minerals with TOC in coastal sediments

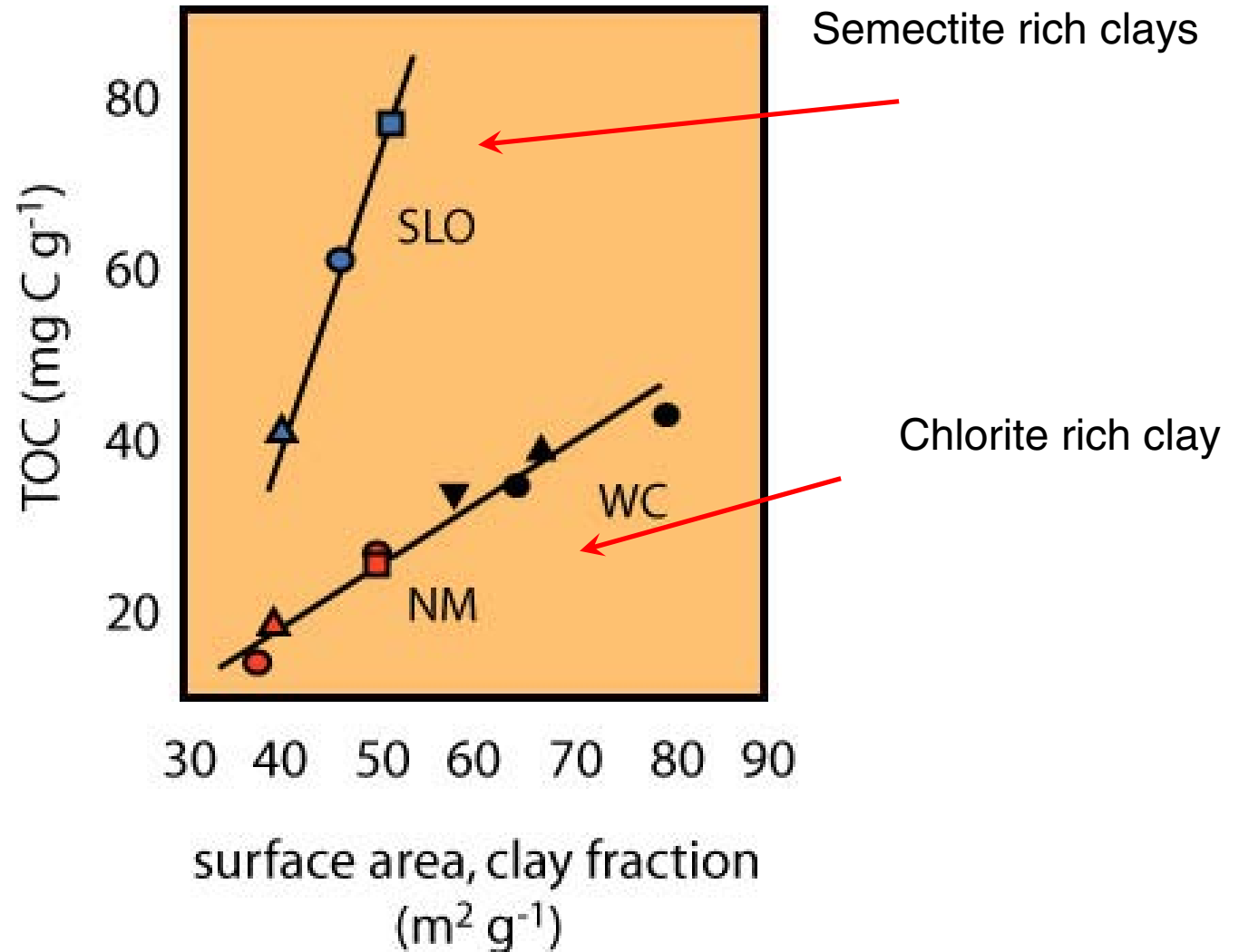
**SLO clays**  
21-29% smectite  
0-3% chlorite

**NM clays**  
3-13% smectite  
13-24% chlorite



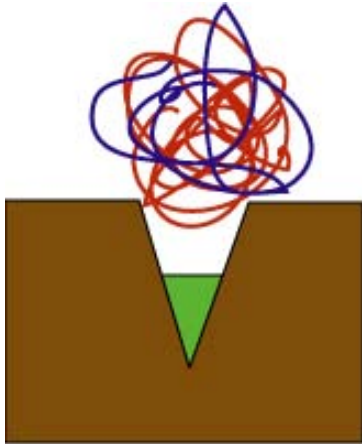
# Clay mineralogy, not simple surface area drives OC preservation

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



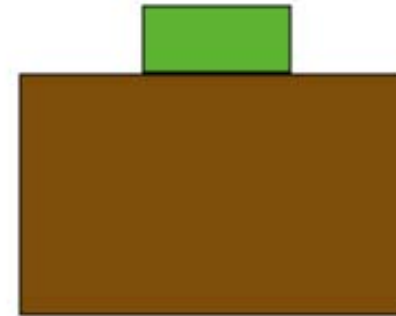
.....and finally the mechanism of preservation....

Mayer-Hedges-Keil hypothesis



Physical protection from enzymatic degradation in small pores/cracks

Ransom hypothesis



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.