### Why is Carbon Preserved in Marine Sediments?

**Enhanced productivity** – More organic matter is produced which leads to a greater flux through the water column and ultimately greater accumulation in sediments. Sediments underlying high productivity areas have higher % OC and higher C accumulation rates:

#### Mechanisms:

Selective preservation – some OM is intrinsically more labile than others Nonselective preservation – a) mineral protection either inside of or on minerals. Enhanced flux due to ballasting. b) reactive OM moves through the high activity sediment/water interface quickly

**Low oxygen**- Less oxygen changes the degradation rate (?) or pathway (?) of C degradation. Mechanisms are not clear, but sediments in low oxygen and anoxic basins have high %OC.

#### Mechanisms:

Anaerobic degradation inherently less efficient than aerobic degradation Anaerobic degradation inherently slower than aerobic degradation poisoning a & b above



#### Relationship between burial efficiency and sedimentation rate



The effect of bottom water oxygen on burial efficiency



Bottom water oxygen (M)

The effect of oxygen on carbon preservation in Maderia Abyssal Plain Turbidites

Before...



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 ( $\beta$ -alanine plus  $\gamma$ -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).

### The effect of oxygen on carbon preservation in continental margin sediments

pp on Mexican shelf < Washington shelf; sedimentation rates are similar; O<sub>2</sub> is very different



Hartnett et al. (1998) Nature v391, 572-574

#### Comparison of Washington and Mexican margin sediments

Table 1 Measured and calculated parameters for Washington and Mexican margin sediments									
	Bottom water O₂ (µmol I⁻¹)	Organic carbon (wt%)	Sediment accumulation rate* (mg cm <sup>-2</sup> yr <sup>-1</sup> )	Organic carbon burial (µmol cm <sup>−2</sup> yr <sup>−1</sup> )	Organic carbon oxidation (µmol cm <sup>−2</sup> yr <sup>−1</sup> )	Burial efficiency (%)	O <sub>2</sub> exposure time (yr)		
Washington									
Shelft									
Average (n = 8)	92.8	1.31	102	117	675	15.1	3.92		
Range	(77–106)	(0.55–1.8)	(61–130)	(28–169)	(506–790)	(3.75–17.8)	(1.1–10.5)		
Upper slope									
Average $(n = 6)$	71.5	1.59	66.9	90.1	316	25.7	6.42		
Range	(38-104)	(0.5-2.8)	(37-100)	(27-210)	(91-607)	(4.69-42.7)	(1.4-14.4)		
Mexico									
Shelf‡									
Average $(n = 4)$	15.4	4.7	14.9	50.9	183	23.3	0.252		
Range	(3-0)	(2.9-7.1)	(9.1-25.6)	(195-392)	(157-200)	(18.8-26.3)	(0.051-0.587)		
Slope	()	(	()	(,	()	(	(,		
Average $(n = 4)$	5.3	10.1	6.87	61.7	91.3	38.2	0.032		
Range	(0.0-12)	(7.5-12.8)	(4.1-12.7)	(160-845)	(55-121)	(19.9-53.1)	(0.0-0.16)		

\*Sediment accumulation rates and wt% OC determinations were made on the same cores; these cores were collected at the stations where benthic flux chamber measurements were made.

† Washington shelf and upper-slope stations had depths in the range 0-200 m and 200-600 m, respectively.
‡ The Mexican shelf extends to ~150 m and the Mexican slope stations range from 150 to 1,000 m.

#### Hartnett et al., Nature 1998

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

Effect of oxygen exposure time on burial efficiency



How does oxygen act to decrease carbon preservation in 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



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.

### 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, 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

# 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...



FIG. 4. Total organic carbon concentration vs. surface area for the refractory background of twenty-two cores from throughout North America. The OC concentration in the refractory background was calculated by fitting downcore data to a two-component decay model (see text). Diagonal bars are the 95% confidence intervals for this data set, and represent the ME zone as defined by the refractory background data. Symbols:  $\Box$ , CHUKCHI;  $\blacklozenge$ , SKAN BAY; O, PUGET SOUND; +, CHESAPEAKE;  $\blacklozenge$ , GULF OF MAINE.

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



### Distribution of mineral pore sizes in marine sediments



#### organic coated particle

### Distribution of mineral pore sizes in marine sediments





ME coating of organic matter

### 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*. Is this evidence for or against physical protection ?







Surface area vs % organic carbon for deltaic and river sediments



12.28

#### 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

Ransom et al., GCA (1998) 62, 1329-1345 12.29

#### 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.)



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



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

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



Ransom et al., GCA (1998) 62, 1329-1345 12.33

.....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.

#### TOC vs surface are 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



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

Oxygen may be a factor

Minerology looks to be very important

The "mechanisms" of carbon preservation are still not understood. Many relationships between %C, sedimentation rate, SA, oxygen, have been shown, but we do not have a mechanistic explanation for why these relationships are observed.

#### Kinetics of organic matter degradation and the multi "G" model





#### Kinetics of organic matter degradation and the multi "G" model





Westrich and Berner, 1984 Berner, 1982

G (mol g-1)

#### Is the "G" model just and observational artifact?



#### 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 10<sup>12</sup> 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.

Mineral surface area and % OC in suspended particulate organic matter and deltaic sediments of the Amazon River



• Suspended particulate matter

• Deltaic particulate matter

Keil et al. 1997 GCA 61 1507-1511

Photographic and experimental evidence shows that organic matter coating onto particles was not even close to an even coverage, that OM is isolated at very specific sites in blobs or blebs





Geochimica et Cosmochimica Acta, Vol. 63, No. 2, pp. 207-215, 1999

12.16