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concentrations in soils and sediments

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(Received May 25, 1993; revision accepted October 4, 1993)

Phil,
Thanks for your help with the soil samples.

Larry





ELSEVIER

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Abstract

Relationships between mineral specific surface area and organic carbon (OC) concentration are examined for sediments and soil A-horizons from throughout the world. I found (published elsewhere) that continental shelf sediments from many different regions exhibit downcore loss of OC to a refractory background level which shows a consistent relationship with mineral surface area (slope = $0.86 \text{ mg m}^{-2} \text{ OC}$). This trend is equivalent to a monolayer of organic matter over all surfaces, and is termed the monolayer-equivalent (ME) level. Sediments and soils from other environments are compared to this empirically derived relationship. Several continental slope areas show extension of this relationship to considerable depth. Marked excesses of OC above this trend, which persist downcore, were found in sediments with high carbonate mineral content or slope sediments with low dissolved oxygen concentrations in the overlying water column. About half of the soils examined also adhered to this relationship, while soils with high carbonate content, low pH, or poor drainage showed OC concentrations higher than the ME level. OC concentrations below the ME level are found in deltaic regions and areas with low organic matter delivery such as the deep sea or arid soils. The nature of mineral surfaces was examined using N_2 adsorption-desorption isotherms, and most surface area was found to be present as pores with $< 8\text{-nm}$ widths. A hypothesis is developed that explains the observed OC concentrations as a saturation of adsorption sites within small pores, which are small enough to exclude hydrolytic enzymes and hence protect organic matter against biological attack. The relationship between this hypothesis and other hypothesized protection mechanisms is discussed. Adsorption is shown to provide a mechanistic and quantitative explanation for spatial and temporal relationships between sedimentation rate and OC burial.

1. Introduction

Many soils and sediments have organic carbon (OC) concentrations in the range of 1–100 mg g^{-1} OC. Observed concentrations are lower than would be expected solely from the relative delivery rates of OC and minerals. Much if not most of the OC delivered to soils and sediments becomes remineralized, accounting for these lower concentrations. At a global scale OC concentrations show a clear positive relationship to or-

ganic matter supply; concentrations are low in deserts and the deep sea, and high in areas of intensive plant production. However, at smaller space scales concentrations often appear to be influenced by factors more related to the preservation of organic matter than to its supply.

OC concentrations in marine continental shelf sediments frequently show a particularly strong correlation of OC concentration with grain size (Premuzic et al., 1982; Romankevich, 1984), especially compared with soils and sediments

from other depositional regimes. In another paper (Mayer, 1994) I have examined the nature of this grain size relationship in terms of the correspondence between OC concentration and mineral surface area of aluminosilicate sediments. In that work I show a widespread, common relationship between OC concentration and surface area that approximates a monolayer of adsorbed OC on mineral surfaces. This relationship provides an explanation for the downcore asymptotic OC concentration (refractory background) found in many shallow-water sediments (Berner, 1982), and hence indicates a surface area control on the stabilization and burial of organic matter in these sediments. A hypothesis was presented to explain this relationship, based on the microtopographic nature of mineral surfaces. In this Symposium paper, I review these shelf data and examine the OC–surface area relationship and the nature of mineral surfaces from a wider range of samples including soils, carbonate sediments and deeper ocean sediments. The OC and surface area relationships found for the shelf sediments are found to have somewhat wider applicability. Some geochemical implications of these widespread relationships are explored.

2. Methods and materials

Samples were obtained from the collections of a large number of investigators (see Acknowledgements). Only unground samples which had been collected recently or stored frozen were obtained. Upon receipt of samples, they were stored frozen in my laboratory. Soil samples were obtained from the National Soil Survey Laboratory (Lincoln, Nebraska, U.S.A.); these samples had been stored at room temperature, but as OC analyses from my laboratory agreed well with their values they were deemed acceptable for the purposes of this study. Prior to analysis, samples were freeze-dried.

To determine the degree of association between organic matter and minerals, some samples were subjected to separations on the basis of density. These separations were performed by

shaking suspensions in saturated CsCl solution ($\rho = 1.9 \text{ g ml}^{-1}$) followed by centrifugation, as described in Mayer et al. (1993).

Sub-samples of most samples were prepared for total OC analysis by grinding and vapor-phase acidification with fuming HCl in a desiccator, to remove carbonate minerals, with sample weights determined before acid attack. Acidified samples were then analyzed on a Carlo Erba® 1106 Elemental Analyzer (precision, as average standard error on duplicates, is $\pm 1\%$). OC analyses were corrected for seasalt contributions to sediment weight. OC concentrations in carbonate sediments from St. Croix, U.S. Virgin Islands, were determined by dichromate titration (Gaudette et al., 1974). The calcium carbonate content of samples from some areas was determined by weight loss after acidification by glacial acetic acid.

For surface area analysis of aluminosilicates, samples were routinely pretreated to remove organic matter using a sodium pyrophosphate–hydrogen peroxide attack. Carbonate samples did not receive this pretreatment. Samples analyzed with and without organic matter removal generally show similar surface area values (Mayer, 1994). Prior to analysis, samples were degassed either for 15 min at a temperature of 250–350°C under a stream of nitrogen–helium or overnight at 150°C in a vacuum oven; similar results were found between these methods. Surface area analysis was usually carried out by the one-point BET* method using N_2 adsorption (analytical precision on duplicates = $\pm 1\%$) with a Quantachrome® Monosorb. This method is described in detail in Mayer (1994). Occasionally a multi-point BET analysis was performed using a Quantachrome® Autosorb 1; multi-point analyses agreed well with single-point analyses.

Pore size distributions on samples were also determined on the Autosorb 1. Samples which had been pretreated to remove organic matter (except the carbonate sample) were degassed at 150°C overnight under vacuum. A full adsorption/desorption isotherm was obtained and the pore size distribution calculated using the man-

*Brunauer–Emmett–Teller adsorption isotherm.

manufacturer's software package. Pore size calculation for mesopores (described below) is based on the Barrett-Joyner-Halenda method (Barrett et al., 1951), in which N_2 condensation is considered to occur within small pores at partial pressures of N_2 below saturation pressure, with the extent of condensation depending on the width of the pore. The data were corrected for multilayer adsorption onto pore walls, using the equation of deBoer et al. (1966), which was chosen based on examination of t -plots of the various samples. The surface area associated with micropores was determined by the t -plot method (Gregg and Sing, 1982).

3. Results

3.1. Previous work

Mayer (1994) has presented a detailed examination of OC accumulation patterns in aluminosilicate sediments of various continental shelf regions. A common pattern described in that work is relatively high OC concentrations at the sediment-water interface underlain by a decrease in concentration to a refractory background level, a pattern well described in the literature (Berner, 1982; Henrichs and Reeburgh, 1987). The largest enrichments of OC at the sediment-water interface were typically found in areas of relatively high organic matter delivery, e.g., inshore sites and polluted areas. Deeper shelf areas typically showed small or no decreases in OC concentration with core depth. These patterns substantiated a trend that can be discerned from the literature (described in Mayer, 1993).

Determination of the OC-surface area relationships of the refractory background showed a consistent relationship for aluminosilicate sediments from all shelf areas except deltaic regions adjacent to rivers with very high sediment delivery rates (e.g., Mississippi River, U.S.A.). Of the 38 continental shelf cores reported in that paper, 22 exhibited OC distributions that could be modelled according to the equation:

$$OC_z = OC_{RB} + OC_{met} \exp(-\beta z) \quad (1)$$

where OC_z and OC_{RB} are the OC concentrations at any core depth z and in the refractory background, respectively; OC_{met} is the amount of metabolizable OC at the sediment-water interface; and β is the depth attenuation coefficient (cm^{-1}). A scatter plot of the OC_{RB} -values thus determined vs. the average surface area values of the deeper core horizons (Fig. 1) showed a highly significant linear relationship ($p < 0.01$) with a slope of $0.86 \text{ mg m}^{-2} \text{ OC}$. The samples from the sediment-water interface, on the other hand, showed much poorer correlation. In other words, regardless of the OC-surface area relationship at the sediment-water interface, the stabilized OC concentration downcore showed a relationship to surface area that was consistent among many different continental shelf areas. Of the cores that did not yield refractory background concentrations by this equation, most had OC concentration-surface area relationships in their deeper horizons that were still consistent with those plotted in Fig. 1.

The significance of this downcore OC-surface area relationship is that it approximates the amount of OC that would be expected from a monolayer of moderate size organic molecules covering all mineral surfaces. For example, proteins typically show OC concentrations of 0.5-1

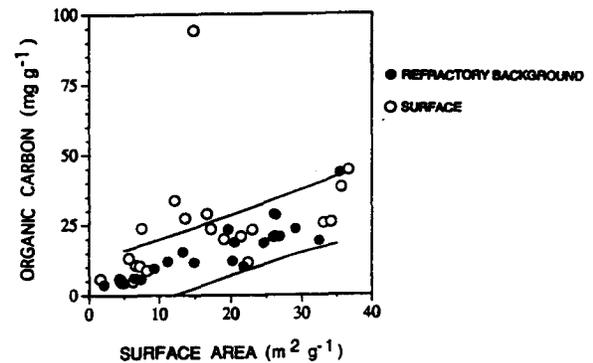


Fig. 1. Concentrations of organic carbon at the sediment-water interface and in the refractory background (calculated according to the algorithm described in the text) of various continental shelf cores in North America. Diagonal bars are the 95% confidence bars for the data (which are different than the 95% confidence limits of the regression line), calculated using the JMP program (SAS Institute, Inc., Cary, North Carolina, U.S.A.).

mg m⁻² OC if adsorbed to monolayer saturation at either solid-water or air-water interfaces (e.g., Arai and Norde, 1990). For this reason, Mayer (1994) applied the term "monolayer-equivalent" to those OC concentrations that fit within the 95% confidence bands of this set of refractory background levels (Fig. 1). Such monolayer-equivalent (ME) coverages have been inferred or determined in other studies as well (Weiler and Mills, 1965; Suess, 1973; Tanoue and Handa, 1979; Keil et al., 1994). The term monolayer-equivalent is stressed, because there is no evidence to indicate that organic matter is indeed wholly dispersed over all mineral surfaces.

The ME level appears to describe the concentration at which OC levels stabilize and become buried in aluminosilicate continental shelf areas other than those adjoining sediment-rich large rivers such as the Mississippi, Amazon (Brazil) and Huanghe (China). An ME range of concentrations, derived from this set of continental shelf cores, can be defined as the 95% confidence intervals about the refractory background data of Fig. 1. Most samples from a much larger collec-

tion of sediment-water interface samples of shelves also plotted within this ME zone (Mayer, 1994). This present work examines the applicability of this ME zone to sediments and soils from other environments.

3.2. Deeper marine sediments

Sediment-water interface samples from ocean depths >200 m (Fig. 2; Table 1) show several features. The ME zone, taken from Fig. 1, extends only to a surface area of ~35 m² g⁻¹, which represents the range of continental shelf samples from which it was calculated. At higher surface area values, the ME zone is likely to level somewhat. Keil et al. (1994) examined grain size separates from Washington, U.S.A., coastal sediments, and found a similar OC-surface area relationship as the ME zone of Fig. 1; above ~40 m² g⁻¹, however, this trend showed a shallower slope. Similar levelling or even drops in OC concentrations have frequently been observed in clay fractions of grain size separations of soils and sediments (Tanoue and Handa, 1979; Tiessen

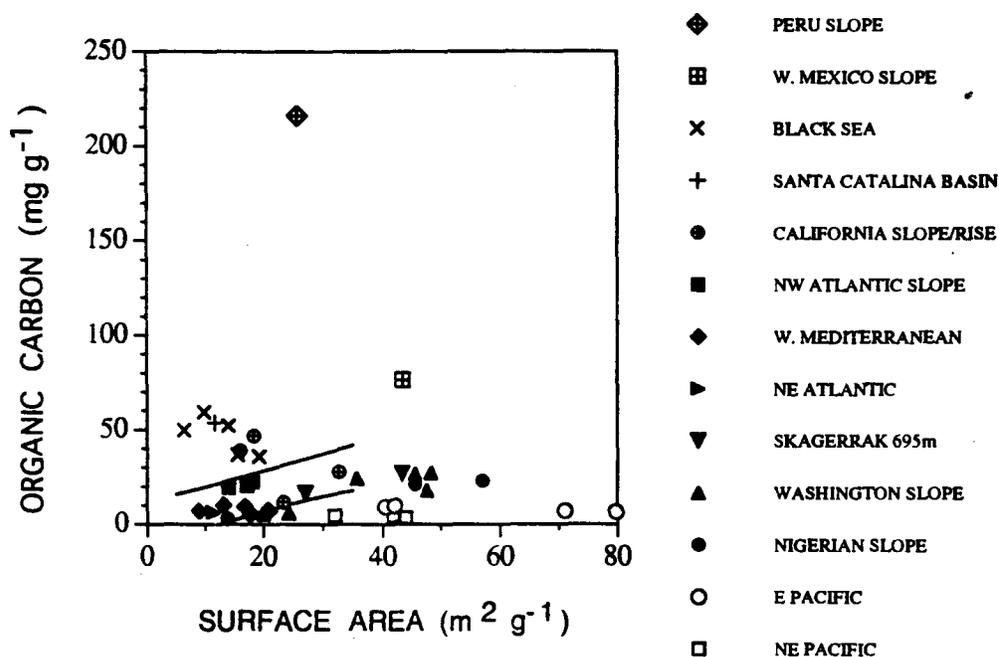


Fig. 2. Organic carbon concentration vs. surface area for samples from the sediment-water interface of deeper marine sediments (slopes, rises and deep sea). Diagonal lines enclose the monolayer-equivalent zone from Fig. 1.

Table 1

Locations, depth of water column overlying sediment along with codes provided by sampler, sampling depth in sediment, organic carbon and surface area of samples from marine deeper water environments, calcium carbonate-rich environments and freshwater environments

(a) Marine slopes, rises and deep sea

Location code	Water depth (m)	Sediment depth (cm)	Organic carbon (mg g ⁻¹)	Surface area (m ² g ⁻¹)	Location code	Water depth (m)	Sediment depth (cm)	Organic carbon (mg g ⁻¹)	Surface area (m ² g ⁻¹)
<i>Northeast Pacific:</i>					<i>NW Atlantic slope (off Maryland, U.S.A.):</i>				
TT183,4-1-2	4,772	0-0.5	4.8	32.0	End187-2	770	1-7	19.5	14.1
TT183,5-1	4,980	0-0.5	4.8	41.7			26-28	20.9	11.3
TT183,6-1	5,668	0-0.5	3.5	43.9			50-57	17.4	11.8
							76-77	14.7	9.5
<i>Washington slope, off U.S.A.:</i>							106-110	11.8	11.2
5	312	0-5	5.4	20.0			125-126	11.4	14.6
6	1,865	0-5	26.7	45.5			150-157	11.9	16.8
7	250	0-5	6.0	24.3			175-176	11.2	19.6
8BC-07	1,900	0-5	27.4	48.3			225-226	7.2	20.6
13BC-09	740	0-5	34.2	35.6					
14BC-10	2,615	0-5	17.9	47.6	End187-3	1,015	2-5	20.7	17.3
							34-35	20.1	18.8
							50-55	18.0	18.3
							75	18.0	18.0
<i>California slope, off U.S.A.:</i>							102-107	17.0	16.8
207	786	0-1	39.1	16.1			135	15.2	18.6
		6-7	37.3	16.0			155	14.0	17.5
		12-14	37.3	21.2			177	12.8	16.5
		18-20	35.3	9.8			203	12.3	16.6
							225	10.9	20.5
213	998	0.5-1	46.8	18.4			248	14.0	18.5
		6-7	46.9	18.2					
		12-14	43.0	15.4	End187-6	1,180	135	37.4	20.8
		18-20	43.4	12.9			240-245	33.4	15.3
221	1,894	0.5-1		35.5					
		6-7	12.7	28.3	<i>NE Atlantic (N. Rockall Trough):</i>				
		12-14	13.1	19.0	NSR-138	1,976	0-2	6.5	11.3
		18-20	12.1	39.3	<i>Skagerrak, Denmark:</i>				
231	3,728	0.5-1	28.1	32.6	D1	695	SWI	16.7	27.1
		5-6	31.6	37.8	D1'	695	SWI	27.2	43.2
		8-10	29.0	38.5	<i>NW Mediterranean Sea,</i>				
238	3,571	0.5-1	12.0	23.4	<i>Valencia-Catalonia, Spain:</i>				
		6-7	18.0	37.9	6	520	SWI	9.5	16.9
		12-14	13.9	27.3	8	1,080	SWI	7.5	21.0
		18-20	12.7	26.9	10	1,790	SWI	6.2	17.7
					<i>Gulf of Lyon, France:</i>				
					12	2,390	SWI	7.1	9.0
					13	2,500	SWI	10.4	13.2
					16	513	SWI	5.3	17.8
					17	800	SWI	7.7	20.9
<i>Santa Catalina Basin, California, U.S.A.:</i>									
1937	2,000	0-1	49.2	11.8					
1938	2,000	0-1	44.0	15.1					
1939	2,000	0-1	48.9	11.8					

er marine sediments

Table 1 (continued)

(a) Marine slopes, rises and deep sea (cont.)

Location code	Water depth (m)	Sediment depth (cm)	Organic carbon (mg g ⁻¹)	Surface area (m ² g ⁻¹)	Location code	Water depth (m)	Sediment depth (cm)	Organic carbon (mg g ⁻¹)	Surface area (m ² g ⁻¹)	
<i>East Pacific:</i>					<i>Black Sea:</i>					
BC-1	4,800	0-0.5	7.3	71.1	Core 6	510	SWI	52.3	14.1	
BC-2	4,800	0-0.5	6.7	79.8	Core 8	564	SWI	59.5	9.9	
MC 19 C6A	3,967	0-0.5	9.2	40.4	Core 10	1,715	SWI	49.9	6.4	
MC 20 C4A	3,920	0-0.5	9.8	42.0	Core 11	1,109	SWI	36.8	15.7	
					Core 12	335	SWI	36.1	19.3	
<i>West Mexico slope:</i>					<i>Nigerian slope:</i>					
NH-15, BC-1	425	0-0.5	76.4	43.4	M-2	483	1.3-6.4	23.0	57.0	
<i>Peru slope:</i>					<i>M-1</i>					
BC 091	309	0-0.5	216.1	25.9		1,085	1.3-6.4	21.2	45.5	
		0.5-5	212.7	27.1			17-22	16.4	59.1	
		5-10	193.8	24.5			45-49	14.4	52.8	
		10-15	123.3	20.0			71-76	18.3	40.1	
		15-20	125.3	15.9			98-103	22.8	35.4	
		20-25	127.0	18.2			131-136	16.4	39.1	
		25-30	140.7	18.8			157-163	13.2	40.3	
		30-35	128.8	16.8			184-189	15.2	37.5	
		35-40	118.5	19.4			221-226	16.3	40.7	
		40-45	110.0	17.7			249-254	15.5	43.5	
		45-50	108.3	18.2			279-284	16.8	44.1	
		50-54	125.9	18.2			302-307	14.4	42.3	
							330-335	15.4	50.2	
							358-363	13.0	57.5	
<i>NW Atlantic Slope (off Maryland, U.S.A.):</i>										
End179-2	1,034	12	22.9	18.1				389-394	15.6	49.9
		102	16.7	18.8				419-424	13.6	62.6
		202	13.5	16.8				442-447	13.3	49.5
End187-4	2,010	12-17	13.0	14.7	M-3	209	1.3-6.4	2.9	13.8	

(b) Calcium carbonate-rich sediments

Sample code	Water depth (m)	Sediment depth (cm)	Organic carbon (mg g ⁻¹)	Surface area (m ² g ⁻¹)
<i>Sugar Bay, St. Croix, U.S. V.I.</i>				
SB1	<3	0-2	49.9	33.1
SB2	<3	0-2	47.1	30.6
SB3	<3	0-2	37.2	25.5
SB4	<3	0-2	33.4	30.4
SB5	<3	0-2	32.5	31.3
SB6	<3	0-2	27.0	29.1
SB7	<3	0-2	17.8	9.5
SB8	<3	0-2	33.1	18.6
SB9	<3	0-2	31.7	14.3
SB10	<3	0-2	5.9	4.0
Stn. 2	20	0-2	4.7	1.1

(c) Freshwater environments

Sample code	Water depth	Sediment depth (cm)	Organic carbon (mg g ⁻¹)	Surface area (m ² g ⁻¹)
<i>Sabine Lake, Texas, U.S.A.</i>				
S-1	n.a.	0-1	6.3	23.1
		1-2	7.9	24.4
		2-3	10.2	33.5
		3-4	8.9	36.3
		4-5	8.7	40.1
		5-6	8.6	38.1
		6-7	13.9	42.9
		7-8	10.7	37.3
		8-9	7.8	29.9
		9-10	7.5	24.5
		10-12	6.5	22.0
		12-14	6.7	19.8
		14-16	7.6	25.2

Table 1 (continued)

(b) Calcium carbonate-rich sediments (cont.)

(c) Freshwater environments (cont.)

Organic carbon (mg g ⁻¹)	Surface area (m ² g ⁻¹)	Sample code	Water depth (m)	Sediment depth (cm)	Organic carbon (mg g ⁻¹)	Surface area (m ² g ⁻¹)	Sample code	Water depth (m)	Sediment depth (cm)	Organic carbon (mg g ⁻¹)	Surface area (m ² g ⁻¹)
6.3	14.1								16-18	8.0	25.4
9.5	9.9								18-20	8.5	31.0
9.9	6.4										
5.8	15.7										
5.1	19.3										
3.0	57.0										
1.2	45.5										
5.4	59.1										
4.4	52.8										
3.3	40.1										
2.8	35.4										
5.4	39.1										
3.2	40.3										
5.2	37.5										
5.3	40.7										
5.5	43.5										
6.8	44.1										
4.4	42.3										
5.4	50.2										
3.0	57.5										
5.6	49.9										
3.6	62.6										
3.3	49.5										
2.9	13.8										
		<i>Salt Bay, St. Croix, U.S. V.I.</i>									
			2	0-1	32.7	35.1	S-2	n.a.	0-1	12.7	30.0
			2	4-5	36.0	38.5			1-2	13.9	32.0
			2	7-8	34.6	40.3			2-3	11.4	28.3
			2	10-12	32.5	36.9			3-4	8.7	25.0
			2	12-14	34.3	39.8			4-5	10.9	34.3
			2	14-17	29.8	26.4			5-6	9.0	25.2
									6-7	9.0	25.1
									7-8	18.4	28.6
									8-9	8.9	22.9
									9-10	11.8	25.0
									10-12	7.3	26.4
									12-14	12.4	26.7
									14-16	11.0	23.7
									16-18	11.4	27.4
									18-20	10.6	26.5
									20-22	9.2	22.0
		<i>S. Florida, U.S.A.</i>									
		F-1	<2	0-2	110.0	15.7					
		F-2	<2	0-2	43.9	8.7					
		F-3	<2	0-2	40.5	8.4					
		F-4	<2	0-2	14.4	3.4					
		F-5	<2	0-2	61.4	7.5					
		F-6	<2	0-2	20.0	6.7					
							<i>Viga River, Brazil</i>	n.a.	0-2	11.8	28.7
									2-4	11.9	23.1
									4-6	10.1	21.1
									6-8	8.1	14.7
									8-10	8.5	13.9
									10-12	14.6	14.9
									12-14	7.3	12.5

SWI refers to sediment-water interface of unspecified depth. n.a. = not available.

Organic carbon (mg g ⁻¹)	Surface area (m ² g ⁻¹)
6.3	23.1
7.9	24.4
10.2	33.5
8.9	36.3
8.7	40.1
8.6	38.1
13.9	42.9
10.7	37.3
7.8	29.9
7.5	24.5
6.5	22.0
6.7	19.8
7.6	25.2

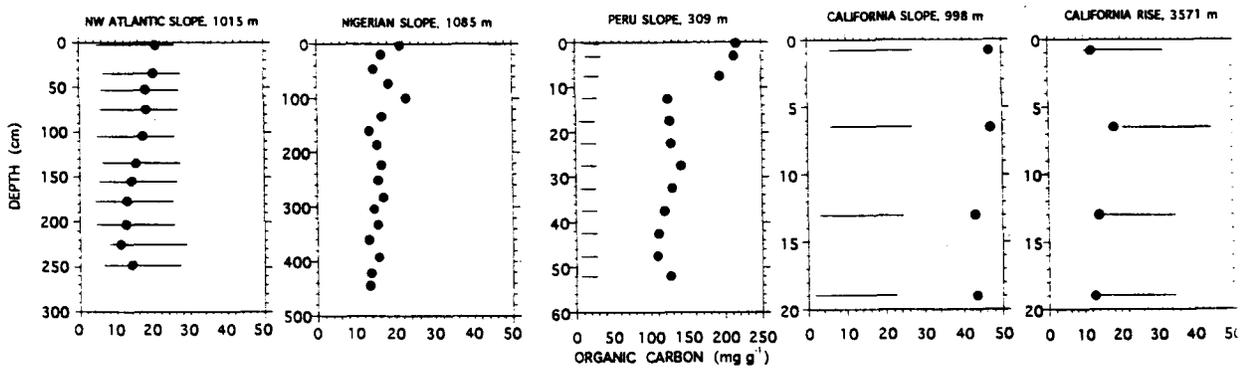


Fig. 3. Organic carbon concentration vs. core depth for cores taken in several slope and rise regions. Solid circles are data points, while the horizontal bars represent the range of the monolayer-equivalent level derived from the 95% confidence bars of Fig. 1, with each range determined for the surface area associated with that depth interval. No such confidence bars could be calculated for the Nigerian slope samples because the surface area values in this core are outside the range of data in Fig. 1.

and Stewart, 1983). Notwithstanding this probable levelling, samples from the deep sea in areas distant from land (eastern and northeastern Pacific) have OC concentrations well below the ME zone. Some hemipelagic sediments near the California shelf, east Pacific, at depths as great as 3728 m, had values within the ME zone. Many of the sediments from slope depths that were sampled in this study [e.g., northwestern and northeastern Atlantic, western Mediterranean and Skagerrak (North Sea)] exhibit OC concentrations within the ME zone, similar to shelf sediments. Some slope sediments with high surface area values, from the Washington and Nigerian slopes, had values which might be within or below the ME zone, depending on the extent to which the ME zone levels as clays become abundant. All samples with values above the ME zone were from areas with low dissolved oxygen concentrations in the water column (Peru, west Mexico, California slope and basin, Black Sea).

Most cores from slope and rise areas showed relatively little downcore change in OC concentration (Fig. 3). The data are plotted with the ME zone indicated by a range bar that represents the upper and lower 95% confidence bounds of Fig. 1. Cores taken in slope areas with low dissolved oxygen concentrations (Peru, California) showed little tendency to exhibit downcore loss of OC to the ME zone, at least within the depths sampled, in contrast to cores from shallow-water, low-oxygen areas such as Skan Bay (Alaska, U.S.A.) which showed OC loss with depth to the ME level (Mayer, 1994). Longer cores (e.g., Nigerian and NW North Atlantic slopes) showed progressive slow decay over 2–4 m, suggesting that the refractory background concentrations of OC commonly found in shorter cores represent only a slowing of OC loss with depth.

3.3. Carbonate sediments

Calcium carbonate-rich samples from coastal Florida, U.S.A., and St. Croix showed OC concentrations generally in excess of the ME level (Fig. 4). The OC loadings were particularly high for the Florida samples, which consisted entirely of CaCO_3 . The St. Croix samples contained 32–

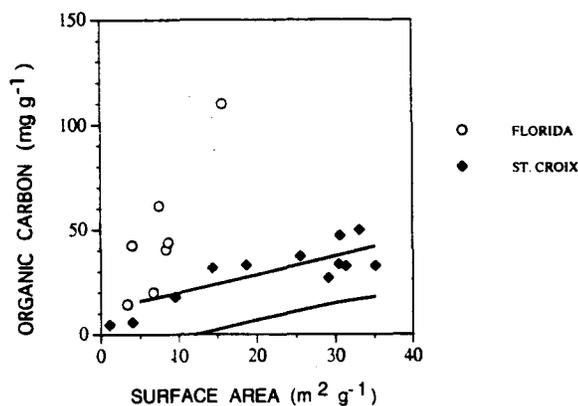


Fig. 4. Organic carbon concentration vs. surface area for samples from the sediment–water interface of calcium carbonate-rich sediments from St. Croix (U.S. Virgin Islands — closed diamonds) and southern Florida (open circles). Diagonal lines enclose the monolayer-equivalent zone from Fig. 1.

97% CaCO_3 , and showed better agreement with the ME zone. One core from St. Croix showed little loss of OC with depth, which contrasts with inshore cores from aluminosilicate-dominated areas (Mayer, 1994).

3.4. Continental environments

Twenty-one A-horizon, soil samples were analyzed (Table 2), a sampling that is not intended to be representative of global soil types. About half of these soil samples yielded OC and surface area values within the ME level (Fig. 5), with other samples falling above and below the ME region. Density separations with 1.9 g ml^{-1} CsCl solutions on thirteen of these samples showed that those samples which plotted above the ME region contained significant fractions of their OC in the low-density fraction (Table 2). On the other hand, almost all of the samples with OC concentrations within the ME zone contained virtually all of their organic matter in the high-density fraction — i.e. the total organic matter was primarily adsorbed to the mineral phase. Soils with OC concentrations in excess of the ME level were a calcium carbonate-rich soil (Texas, U.S.A.), three acidic soils [Tennessee (U.S.A.), Florida (U.S.A.) and Cascade Head (Oregon,

Table 2
Soil descriptions and data

Location	Description	Sample code	Surface area (m ² g ⁻¹)	Organic carbon (mg g ⁻¹)	Soil pH	Fraction of OC in high- density phase
Idaho, U.S.A.	typic Cryaquept	88P0072	37.4	21.9	7.7	0.95
Texas, U.S.A.	thermic Caliustoll	88PP667	29.1	50.5	7.0	0.86
New Mexico, U.S.A.	aridic Haplustalf	88B728	34.7	11.5	7.3	0.89
Indiana, U.S.A.	typic Hapludalf	88P797	18.6	8.1	7.1	0.91
Tennessee, U.S.A.	typic Hapludalf	88B1699	6.0	50.0	4.1	0.64
Illinois, U.S.A.	typic Hapludalf	88P2173	4.4	6.5	4.2	0.94
Maryland, U.S.A.	typic Dystrachrept	88P2535	23.3	9.6	6.5	0.90
Ohio, U.S.A.	typic Hapludalf	88P3584	14.9	16.5	7.2	0.86
Oklahoma, U.S.A.	typic Ustrochrept	88P3889	12.6	15.5	8.0	0.65
Iowa, U.S.A.	typic Hapludoll	88P2870	13.9	10.3	7.5	0.94
North Dakota, U.S.A.	typic Argiboroll	87P2978	21.5	17.6	7.9	0.98
California, U.S.A.	typic Argixeroll	87P3636	30.5	30.0	6.2	0.66
Maine, U.S.A.	fluvaquentic Humaquept	MedA	14.5	115.4	n.a.	0.54
Florida, U.S.A.	ultic Haplaquod		0.1	18.5	3.6	
* Cascade Head, Oregon, U.S.A.	typic Dystrandept		33.5	172.5	4.3	
Konza, Kansas, U.S.A.	pachic Argiustoll		18.0	31.2	6.4	
* Andrews, Oregon, U.S.A.	andic Haplumbrept		20.5	49.1	6.1	
Wind River, Washington, U.S.A.	andic Haplumbrept		13.0	18.5	n.a.	
LaSelva, Costa Rica	fluventic Eutropept	LT, 1-5 to 4-5	26.7	28.0	n.a.	
LaSelva, Costa Rica	oxic Dystropept or oxic Humitropept	UT, 5-5 to 8-5	60.7	38.4	n.a.	

All samples are A-horizons. Reported soil pH data based on 1:1 H₂O mixtures. Fraction of OC in high-density phase was calculated as the concentration of OC in the high-density phase divided by the concentration in the unfractionated soil. n.a. = not analyzed.

U.S.A.)], a poorly drained soil (Maine, U.S.A.), an andosol (Andrews, Oregon, U.S.A.) and a prairie ustoll (Kansas, U.S.A.). The only sample

with an OC concentration clearly below the ME level was an arid soil (New Mexico, U.S.A.). Data from the literature are consistent with my

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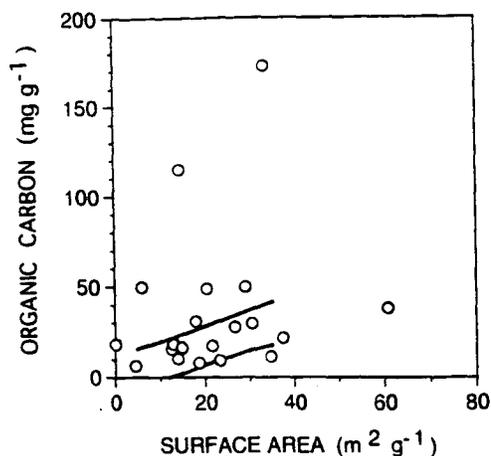


Fig. 5. Organic carbon concentration vs. surface area for soil samples; data are in Table 2. Diagonal lines enclose the monolayer-equivalent zone from Fig. 1.

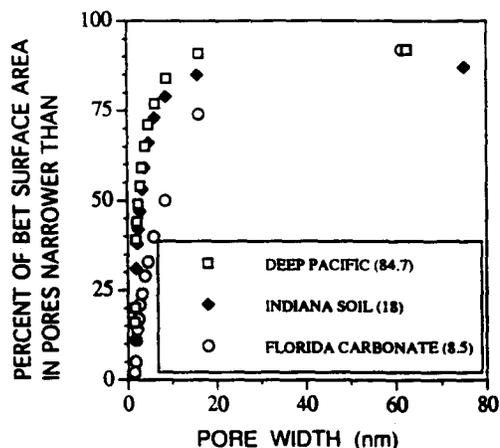


Fig. 6. Percent of BET surface area vs. pore width in mineral grains from a deep Pacific sediment, a soil from Indiana and a carbonate sediment from Florida. The y-axis show the cumulative percentage contained in slit-shaped pores narrower than the x-axis value. Plotted values contain contributions from micropores. Total surface area values, from BET analysis, of these samples are given in parentheses, and represent the 100% y-axis value. Pore size distribution was calculated from the N_2 desorption isotherm.

results. Eight of twelve A-horizon samples reported by Gallez et al. (1976), Borggaard (1979, 1982), and Feller et al. (1992) yielded values within the ME zone. Literature data using surface area analyses other than the N_2 BET method

were ignored, due to lack of comparability between methods.

Little attempt was made to sample freshwater environments for this study. Two cores were obtained from Sabine Lake, Texas, and one core from the Vigia River in Brazil (Table 1). All three cores show OC concentrations below the ME level, with little change downcore in OC concentration relative to this level. From the literature, Ball et al. (1990) examined grain size separates of an aquifer sand, considered to be a former lacustrine deposit, and Baccini et al. (1982) examined a modern lake sediment. In contrast to my findings, their data are within the ME zone.

3.5. Nature of mineral surfaces

The surface area of minerals found in soils and sediments is considerably higher than would be predicted from grain size (Weiler and Mills, 1965), due to surface roughness of the mineral particles. This surface roughness can be expressed in terms of a pore size distribution, by calculating the surface area associated with pores of different sizes (micropores are <2 nm, mesopores are 2–50 nm and macropores are >50 nm in width). The most common method to measure the mesopore size distribution is to examine N_2 condensation at intermediate partial pressures. Assumptions and other details for these measurements and calculations are presented in Mayer (1994). Most adsorption-desorption isotherms had narrow hysteresis loops indicative of slit-shaped pores, as found by Greenland and Mott (1978) and Titley et al. (1987). The instrument's software calculates pore sizes assuming cylindrical pores, but the radii of cylindrical pores can be regarded as equivalent to the width of slit-shaped pores (Innes, 1957) and are presented here as slit widths.

Pore size distributions were calculated for this study using the desorption leg of the adsorption-desorption isotherm. Although either leg may be used for such calculations, slit-shaped pores likely have a delay in condensation during the adsorption leg and hence can give misleading results. Further, excellent agreement was found between

Table 3
Pore size data for soils and sediments

	BET surface area ($\text{m}^2 \text{g}^{-1}$)	Micropore surface area ($\text{m}^2 \text{g}^{-1}$)	Total mesopore surface area		Sum (micropore + desorption mesopore area) ($\text{m}^2 \text{g}^{-1}$)	Fraction of BET surface area in < 8-nm pores
			adsorption ($\text{m}^2 \text{g}^{-1}$)	desorption ($\text{m}^2 \text{g}^{-1}$)		
<i>Sediments:</i>						
Nigerian slope	40.7	0.0	27.5	40.6	40.6	0.84
Florida carbonate, U.S.A.	8.5	0.0	6.5	7.8	7.8	0.48
NW Atlantic	19.3	2.2	13.7	19.0	21.2	0.94
E. Pacific	84.7	11.1	46.3	67.0	77.1	0.82
California slope, U.S.A.	34.2	3.8	20.0	30.0	33.8	0.86
Puget Sound, Wash., U.S.A.	27.3	2.1	17.5	26.0	28.1	0.94
Skagerrak, Denmark	14.2	1.4	10.2	13.1	14.5	0.77
Huanghe Delta, China	25.3	0.1	14.9	20.0	20.1	0.63
<i>Soils:</i>						
Cascade Head, Oreg., U.S.A.	17.7	0.0	13.8	29.6	29.6	1.60
Indiana, U.S.A.	18.0	1.3	10.3	14.3	15.6	0.77
Ohio, U.S.A.	13.5	0.8	7.3	12.3	13.1	0.89
Oklahoma, U.S.A.	21.8	0.2	8.0	15.5	15.7	0.70

BET surface area calculated from multi-point adsorption data. Micropore surface area calculated from t -plots. Total mesopore surface areas calculated from adsorption and desorption legs of isotherm and are integrated over entire mesopore range. The sum of the surface areas from the micropores and mesopores (calculated from the desorption leg) agree well with the BET surface area, which measures all surfaces. The last column gives the ratio of surface area found in micropores and mesopores < 8 nm in width (from the desorption leg) to the BET surface area.

the BET surface area values and the sum of the cumulative surface area from the desorption isotherm plus the surface area from micropores (Table 3). Poorer agreement was found using the adsorption leg. The major exception to this agreement was the Cascade Head soil, which had 60% more area from the sum of mesopores and micropores than was obtained by BET analysis. This sample showed an abnormally large adsorption-desorption hysteresis, which suggests network effects during desorption that cause overestimates of surface area (Lowell and Shields, 1984). The hysteresis is similar to that observed for halloysite (Gregg and Sing, 1982), and perhaps indicates tubular minerals such as imogolite, a common constituent of andosols.

All samples examined in this study showed the total surface area to be dominated by smaller mesopores (2-8-nm width) and micropores (< 2 nm), especially the former (Fig. 6; Table 3). No sample showed more than 13.1% of its surface area in micropores. Macropores (> 50 nm) are generally unimportant contributors to surface area, based on two continental shelf samples

analyzed commercially by mercury porosimetry (Lowell and Shields, 1984), in addition to the excellent agreement between BET analyses and the sum of micropore and mesopore areas. These data are consistent with results of Greenland and Mott (1978), Titley et al. (1987), and Murray and Quirk (1990a, b). No systematic trends were found with sample location. The carbonate sediment had a considerably lower fraction of its surface area associated with small mesopores than any of the aluminosilicate samples. Experiments testing the effect of the hydrogen peroxide attack showed that these results are not an artifact of that step.

4. Discussion

The data presented in Mayer (1994) show that the ME zone defines a relationship between OC concentrations and surface area that is remarkably consistent for aluminosilicate sediments of continental shelf regimes away from major sediment-carrying rivers. Moreover, most of the up-

per slopes and rises adjacent to shelves show "draping" of this ME relationship to considerable depth (e.g., California and NW North Atlantic slopes), though several samples may show sub-ME levels of OC. In areas of low dissolved oxygen concentration the OC concentrations commonly exceed the ME level. In shallow-water areas this enrichment decreases downcore to the ME zone within tens of cm, whereas in slope sites this enrichment appears to persist downcore. In deltaic regions the OC concentrations are generally below the ME level (Mayer, 1994).

Carbonate sediments were sampled only in areas within a few meters of shore, and were generally found to contain OC in excess of the ME level. This finding may result from the sampling bias toward very shallow water. The persistence of OC downcore suggests a greater stabilization of OC than is found in comparable aluminosilicate sediments, perhaps due to incorporation of organic matter within the mineral matrix. On the other hand, Suess (1973) found size separates of a lagoonal carbonate sediment to contain ME levels of OC. It is premature to infer patterns of OC relative to the ME level in carbonate sediments.

Consistent patterns of OC accumulation relative to the ME zone in soils are also not clear, due to the small number of samples analyzed. The data presented here and in the literature are at least consistent with the pattern:

- about half of the soils reported here and in the literature are within the ME zone;
- a group of soils with OC concentrations above the ME zone are in environments thought to have particular stabilization mechanisms for organic matter (e.g., acidic, allophanic and poorly drained soils), or in a carbonate soil which shows an enrichment analogous to the marine carbonate samples;
- OC concentrations below the ME zone are in an arid region of low organic matter production, analogous to the deep-sea samples.

Clearly more data are needed to establish the applicability of the ME zone to soils. The OC concentrations of *A*-horizons commonly fall into the 5–40 mg g⁻¹ OC range that is typical for the ME level. Regional soil surveys often show strong

correlation with grain size as measured by clay content (e.g., Spain et al., 1983; Nichols, 1984). The clay content, expressed as percent, is numerically similar to its surface area, expressed as m² g⁻¹ (Mayer and Rossi, 1982). Regionally tight relationships between OC concentration and percent-clay reported in the literature (e.g., Nichols, 1984; McDaniel and Munn, 1985) thus suggest a more widespread adherence to the ME zone in soils such as mesic Mollisols. An additional, complicating factor in many soil *A*-horizons is vascular plant detritus, which can contribute significant amounts of non-adsorbed organic matter.

Hence it seems that the ME level is a remarkably common, though far from universal, relationship between OC concentration and surface area in aluminosilicate sediments and soils. The ME level seems to be particularly common in aluminosilicates on continental platforms (i.e. soils, shelves and upper slopes) that receive moderate delivery of organic matter and are not subjected to oxygen depletion or low pH. Furthermore, density separation data presented here for soils and in Mayer et al. (1993) and Mayer (1994) for sediments indicate that organic matter is primarily adsorbed to the mineral phase. What mechanism might link OC concentration and surface area?

4.1. Hypothesis

The pore size distribution data (Table 3; Fig. 6) may provide a clue to such a link. Most of the surface area of all of the aluminosilicate sediments and soils measured is in the form of very small mesopores and micropores, a fact generally unappreciated in the literature. If present in a highly dispersed state such as a monolayer, then organic coatings on mineral grains most likely reside in these small pores. Hydrolytic enzymes, which are responsible for the initial step in organic matter decay, are unable to enter pores of smaller than about twice their major axis (Messing, 1974). This size exclusion of enzymes ought to prevent even the smallest of hydrolytic enzymes, with molecular weights of 10–20 kD and major axis lengths of ~4 nm (Arai and Norde,

1990), from entering pores smaller than 8 nm, which contain most of the surface area in soils and sediments. Most hydrolytic enzymes are larger than 10–20 kD, with larger exclusion sizes. Therefore, if the enzymatic hydrolysis of macromolecules to smaller oligomers or monomers is the rate-limiting step in the metabolism of sediment or soil organic matter, it follows that at least a kinetic inhibition of organic matter decay will occur if the organic matter is adsorbed into small pores.

The correlation of OC concentration with surface area that defines the ME zone (Fig. 1) may therefore represent a maximum adsorptive capacity of minerals for organic matter that can be protected by enzyme exclusion. This saturation of protected adsorption sites may explain the common grain size correlation with OC concentration found for shelf environments, which do show saturation, but not for deep-sea environments (Premuzic et al., 1982; Romankevich, 1984), which are below saturation. Samples with OC concentrations below the ME zone may still be protected in a like manner, but simply have not built up organic coatings to ME levels. We therefore find sub-ME levels of OC in soils and sediments with low organic matter delivery rates (arid regions, deep sea) or in areas with rapid sedimentation rates that prevent long-term exposure to organic inputs (e.g., deltaic regions). Within an area of sub-ME levels of OC such as the deep sea, it is therefore reasonable to find OC concentrations proportional to organic matter delivery rates (i.e. primary production rates in the overlying water column).

Evidence for pore protection in sediments with sub-ME levels of OC is the fact that cores with such levels do not show rapid decreases in OC concentration near the sediment–water interface (e.g., Mississippi Delta, Nigerian slope, Sabine Lake). In no core examined in this study or Mayer (1994) was there rapid decrease in OC with depth in the core once the OC concentrations were at or below the ME level. However, longer cores such as those from the NW North Atlantic and Nigerian slopes show that stabilization at the ME level is but a slowing of decay, not a complete cessation. Future work should as-

sess decay constants for OC in the context of the ME zone.

The ME level defines the OC concentration at which downcore loss of OC slows markedly in most continental platform cores collected at sites with oxygenated water columns. In coastal areas with low dissolved oxygen levels in the water column [Skan Bay (Alaska, U.S.A.), Chesapeake Bay (Maryland, U.S.A.), Saanich Inlet (British Columbia, Canada); Mayer, 1994], the OC levels also decreased to ME levels within depths of tens of cm, while in slope areas with low dissolved oxygen levels (California, Peru) OC did not approach the ME level. In these latter areas there is presumably some other means of protection of organic matter at levels higher than the ME zone, which is overcome in the shallower areas. The nature of such a protection mechanism is beyond the scope of this paper, but use of the ME zone allows its identification.

Many hypotheses have been put forward to explain the stability of organic matter in soils and sediments. These hypotheses are frequently based on selective preservation of a refractory component of the original biochemical compounds (e.g., lignins, cutins), formation of heteropolycondensates (humification), or some form of physical protection such as adsorption. Each type of stabilization may operate to some extent in different environments [reviewed in Henrichs (1992)]. However, stabilization by the first two categories of protective mechanism — selective preservation and condensation — cannot by themselves explain the surface area dependence of OC concentrations found so frequently. This surface area dependence implies some critical role for adsorption.

The literature on the effects of adsorption on bioavailability is ambiguous. Many studies have demonstrated a reduction in bioavailability of organic molecules upon adsorption to mineral surfaces. Greatest inhibition has been observed with minerals such as expandable clays or allophanic materials (Pinck et al., 1954; Kobayashi and Aomine, 1967; Greaves and Wilson, 1973), though even clay-free sand has been shown to stabilize organic compounds (Lorenz and Wackernagel, 1987). However, adsorbed organic ma-

cromolecules can be attacked by hydrolytic enzymes and made available for biological uptake (Estermann et al., 1959; Greaves and Wilson, 1970; Samueisson and Kirchman, 1990). Incorporation into small pores offers a mechanism by which adsorptive protection can be effective, and perhaps explain these inconsistencies in the literature.

Pore exclusion of enzymes differs from other matrix protection hypotheses. The long-hypothesized role of interlamellar adsorption in expandable clays appears to have a role in decadal stabilization of organic matter (Ensminger and Gieseking, 1942; Sorensen, 1967), but soils and sediments with high concentrations of expandable clays do not show enhanced OC concentrations consistent with the very high interlamellar surface areas ($760 \text{ m}^2 \text{ g}^{-1}$) of these minerals. Interparticle porosity (in contrast to the intraparticle porosity measured in this study) has been hypothesized to exclude bacterial cells and hence their access to organic molecules (van Veen and Kuikman, 1990). The interparticle pore sizes necessary to exclude bacterial cells are two orders of magnitude larger than the intraparticle pores necessary to exclude their hydrolytic enzymes. In both the expandable clay and interparticle pore hypotheses, the pores are eventually expandable and hence accessible. Intraparticle pores are not expandable, and can provide a greater capability for long-term organic matter protection. Clay fractions of sediments, in fact, appear to contain less organic matter per unit of measured surface area than tektosilicate fractions (Keil et al., 1994).

A prerequisite for effective stabilization of organic matter by incorporation into small pores is that adsorbed molecules remain in the pores. Organic molecules that easily desorb will become available for hydrolytic attack in solution and hence show little preservation. Adsorptive protection of organic molecules may require either condensation to create strongly adsorbed molecules, or selection for original biochemicals that have this property. In this manner the adsorption protection hypothesis may operate with other stabilization mechanisms, rather than in place of them.

Long times may be required to accumulate these strongly adsorbed organic molecules. Soil chronosequences typically indicate that OC concentrations in the A-horizon require decades to millennia before reaching, and stabilizing at, values suggestive of ME levels (Sollins et al., 1983; Birkeland, 1984). Similar time sequences are more difficult to find in sediment systems, because organic-free mineral surfaces are not generally placed into depositional situations. Data from samples of deltaic origin demonstrate that OC concentrations below the ME level (Mayer, 1994) are not built up to ME levels within the time allowed by the rapid sedimentation rate of these systems. Slow build-up of organic matter protected by adsorption into mesopores is consistent with the paucity of the common biochemicals (proteins, carbohydrates) in bulk sedimentary organic matter, and points toward involvement of some kind of slower process like condensation reactions or selection for a minor, refractory, biochemical constituent. The great age of organic matter in many recent sediments and soils — $\sim 10^3$ yr (e.g., Scharpenseel, 1977; Walsh et al., 1985) — is further evidence for slow accumulation. The lack of build-up to ME levels in deep-sea sediments indicates, however, that time is not the only factor; some minimum rate of organic matter delivery in conjunction with sufficient time must be necessary to achieve saturation of protected sites.

Adsorption into small pores might promote successful condensation reactions because: (1) some condensation reactions are both kinetically and thermodynamically favored when the reactants are adsorbed (Wächtershäuser, 1988); and (2) adsorption into small pores may provide a site where slower condensation reactions can occur because of exclusion of faster, competitive biological reactions, as suggested for melanoidin formation in bone tissue (Collins et al., 1992).

4.2. Geochemical implications

The data presented here indicate that many aluminosilicate soils and sediments show stabilization of OC concentrations at a level related to the total surface area of the minerals. The pore

to accumulate molecules. Soil data that OC require decades to stabilize at, (Sollins et al., 1992) in sediment systems, surfaces are not in all situations. can demonstrate the ME level up to ME levels rapid sedimenta-build-up of or- into meso- paucity of the eins, carbohy- anic matter, and some kind of reactions or se- iochemical con- matter in many $\sim 10^3$ yr (e.g., 1985) — is a function. The lack of sea sediments in- the only factor; matter delivery me must be nec- protected sites.

might promote ons because: (1) e both kinetically d when the reac- user, 1988); and s may provide a reactions can oc- ster, competitive d for melanoidin ns et al., 1992).

indicate that many nents show stabi- at a level related nerals. The pore

size data provide a possible reason for this ap- parent stabilization, via the hypothesis of hydro- lytic enzyme exclusion. Regardless of the verac- ity of the enzyme exclusion hypothesis, the fact that OC concentrations are so tightly coupled to surface area has important implications. First, the ability of some soils to accumulate standing stocks of OC, or of depositional environments to bury OC to depths of $\sim 10^1$ – 10^2 cm, may be di- rectly related to the surface area of the constitu- ent minerals. This surface area is largely created by disaggregation of rocks and corrosion of min- eral surfaces. At geological time and space scales, OC accumulation and burial will be limited by the rate of creation of adsorptive mineral sur- faces. This rate will in turn be controlled by nu- merous factors, with tectonics controlling at large space and time scales. This control can explain, for example, the spatial correlations between sedimentation rate and OC burial rate [though it is not the only explanation; see review in Ingall and van Capellen (1990)]. The temporal asso- ciation of OC burial with tectonic activity and hence sedimentation rates since the Archean (Des Marais et al., 1992) is a further example. The pore protection hypothesis provides a me- chanistic explanation for this covariance, in con- trast to most explanations that rely on covari- ance of both organic matter and mineral accumulation rates on a third factor such as water depth or proximity to shore.

Surface area control of OC concentration can explain the relative carbon burial flux via OC vs. mineral carbonate sedimentation since Precam- brian times (Schidlowski, 1988; Des Marais et al., 1992). The ratio of these two flux terms is about 1:4 in the latter half of Earth history. As- suming that surface area provides a cap on OC burial flux, then this flux ratio can be predicted from the ratio of surface area generated by weathering to the amount of dissolved Ca deliv- ered to the ocean. The supply of adsorptive sur- faces can be estimated as the product of the pre- agricultural riverine flux of sediment to the oceans — ~ 200 mg l^{-1} sediment (Milliman and Syvitski, 1992) and an average surface area of 15 m² g⁻¹ (the approximate mid-point of the shelf sediment values from Fig. 1). Assuming an

ME level of OC (~ 10 mg g⁻¹ OC, from Fig. 1), riverine sediment can then lead to 0.167 mmol OC burial per liter of river water flux. The average riverine dissolved Ca concentrations of 0.375 mM, to which can be added the equivalent of 0.066 mM from hydrothermal inputs of Ca to the ocean, can then allow 0.44 mmol C per liter of river water flux to precipitate as carbonate min- erals. The ratio derived from surface area and dissolved Ca is thus 1:2.6, similar to the ob- served ratio of 1:4. The calculation could be re- fined by using the appropriate average surface area of weathered minerals, the appropriate value of OC relative to the ME level in average buried sediment (a sub-ME level of OC, as found for deltas, is likely more appropriate), incorpora- tion of Mg into the carbonate minerals, and so forth.

An intriguing question that arises as a result of ME levels of OC in both soils and continental shelf sediments is the degree to which OC in shelf sediments represents new carbon storage. Shelf sedimentary OC may contain significant contri- butions from terrigenous OC [reviewed in Hedges (1992)], so that shelf burial loses some importance as a sink for carbon derived from the marine environment. If shelf sedimentary OC is indeed primarily marine, then the terrigenous OC must have been somehow displaced by marine OC. It is not known if riverine sediment deliv- ered to the ocean contains an ME level of OC. Keil et al. (1994) found suspended sediment from the Columbia River (Washington) to have OC concentrations at the ME level, though the riverine sediments presented here have lower concentrations. Although the soil samples in this study frequently showed ME levels of OC, river- ine sediment may be derived extensively from soil horizons below the A-horizon and therefore have, on average, sub-ME levels of OC. These possibilities require further examination before the net role of ocean margin sedimentation in the carbon cycle can be assessed.

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