Pergamon

Geochimica et Cosmochimica Acta, Vol. 68, No. 19, pp. 3863-3872, 2004

0016-7037/04 $30.00 + .00

doi:10.1016/j.gca.2004.03.019

Organic matter in small mesopores in sediments and soils

LAWRENCE M. MAYER,[1,*] LINDA L. SCHICK,[1] KATHLEEN R. HARDY,[1] ROTA WAGAI,[1] and JOHN MCCARTHY[2]

[1]Darling Marine Center, University of Maine, Walpole ME 04573 USA
[2]Department of Geological Sciences, University of Tennessee, 306 Geology Building, Knoxville, TN 37996 USA

(*Received September* 8, 2003; *accepted in revised form March* 24, 2004)

Abstract—The three-way correlation among organic matter concentrations, specific surface area and small mesopores observed for many soils and sediments led to the hypothesis that enclosure within the pores might explain the apparent protection of organic matter by minerals. We test this hypothesis by examining whether the bulk of organic matter resides within small mesopores. Pore volumes as a function of pore width were measured before and after organic matter removal, and the volume differences ascribed to organic matter filling of pores. Minor changes in small mesopore size distributions upon treatments such as centrifugation and muffling indicate the robustness of the mineral matrices that form these pores. We developed an additional method to assess organic matter densities using high-resolution pycnometry, and used these densities to convert pore volumes to organic matter contents. Although smaller mesopores are shown to have sufficient volumes to contain significant fractions of the total organic matter, only small fractions of total organic matter were found to reside in them. These results are consistent with preferential association between organic matter and aluminous clay particle edges, rather than the largely siliceous clay faces that contribute most surface area and form pore walls. While simple enclosure within smaller mesopores cannot, therefore, explain protection, network effects working at larger size scales may account for exclusion of digestive agents and hence organic matter protection. *Copyright © 2004 Elsevier Ltd*

1. INTRODUCTION

Significant amounts of organic matter in soils and sediments appear to be protected against biologic remineralization (Hedges and Oades, 1997). Hypotheses to explain this protection include variations on the themes of chemical recalcitrance (i.e., cross-linking by bonds that are not hydrolyzable by biota), availability of certain oxidants, or physical protection by aggregation with minerals (e.g., Sollins et al., 1996). The last mechanism is strongly suggested by a common association between organic matter and fine-grained clay minerals, which has been shown via several lines of evidence. One of these lines is a series of correlations between organic matter concentrations and specific surface area of the mineral fraction (Mayer, 1994a; 1994b; Ransom et al., 1998; Kahle et al., 2002). The specific surface area of soils and sediments generally correlates strongly with fine clay abundance (e.g., Mayer and Rossi 1982). The amount of organic matter associated with clays is often parameterized as a ratio of organic carbon to specific surface area (OC:SFA). Most organic matter buried in the oceans has OC:SFA values of 0.2–1.2 mg-organic carbon m^{-2} (Mayer, 1994a, 1995; Hedges and Keil, 1995). This range of OC:SFA ratios also pertains to many soils (Mayer, 1994b).

Specific surface area also correlates well with the presence of small pores, called mesopores, of size range 2–50 nm. Most of the surface area of many soils and sediments is associated with smaller mesopores of size less than 8 nm (Mayer, 1994b). Such small pores can exclude penetration by enzymes that are necessary to initiate organic matter decay (Zimmerman et al., 2004). The correlations among organic matter, surface area, and small mesopores stimulated the hypothesis that the organic matter in these mesopores is protected against enzyme attack, and hence subsequent remineralization, by physical exclusion of the enzymes (Adu and Oades, 1978; Mayer, 1994a).

Hydrolytic enzymes are proteins that can be as small as 3–4 nm (e.g., Diaz and Balkus, 1996). If organisms are able to make enzymes this small, then it follows that only pores smaller than this size should be able to protect organic matter against all enzymatic attack. While many enzymes are considerably larger, the most conservative form of this hypothesis would imply that pores smaller than several nm (i.e., able to exclude all known enzymes) hold major fractions of organic matter in soils and sediments.

How much organic matter can be or is held within mesopores small enough to protect organic matter against enzyme attack? Previous work showed that organic matter was not present as a continuously dispersed monolayer, and is instead present as more discrete blebs (Mayer, 1999). Are these blebs present within small mesopores? Attempts using electron microscopy to pinpoint the location of sedimentary organic matter have lacked the requisite combination of spatial resolution and elemental analytical capability to answer this question quantitatively (e.g., Ransom et al. 1997; Furukawa, 2000).

We therefore tested the holding capacity of mesopores by assessing the pore volumes available at various pore sizes in the mesopore size range, using gas sorption analysis. We also tested for the presence of organic matter in these mesopores by measuring pore volume distributions before and after organic matter removal, on the assumption that the difference in pore volumes could be assigned to the organic matter. To test for analytical artifacts due to the process of organic matter removal, we examined changes in pore size distribution of the mineral framework using Small Angle X-ray Scattering (SAXS), which provides an independent and complementary view of pore size structure.

* Author to whom correspondence should be addressed (Lmayer@maine.edu).

Table 1. Sample data table.

Sample location	Depth (cm)	Organic carbon (mg g^{-1})		Surface area (m^2 g^{-1})		OC:SFA (mg·OC m^{-2})	ρ_{OM} (g cm^{-3})
		Unmuffled	Muffled	Unmuffled	Muffled		
MARINE SEDIMENTS							
Low Organic Loading							
Equatorial Pacific, 4900 m	SWI	6.7	1.0	105.0	88.1	0.08	1.43
Amazon Shelf Core (Brazil) 4221-1	Composite	5.9	1.2	52.8	38.3	0.15	1.58
Moderate Organic Loading							
Skan Bay, AL	10–12 cm	44.9	2.5	26.1	48	0.94	1.23
Ecl River shelf, CA, Composite	SWI	10.5	1.5	14.1	16.9	0.62	1.34
Bering Sea shelf, AL, KS-22	SWI	5.9	1.2	8.9	7.4	0.80	n.d.
San Diego Harbor, CA, SS 1,2	SWI	15.6	2.3	13.9	16.7	0.93	1.68
Pemaquid, ME	14–36 cm	20.2	4.1	33.8	25	0.81	1.14
Damariscotta estuary, ME	SWI	23.2	3.7	32.9	33.8	0.69	n.d.
Lowes Cove intertidal, ME	SWI	10.9	1.2	8.4	6.8	1.60	1.86
Little River intertidal, GA 6	SWI	50.5	6.2	33.4	45.1	1.12	1.25
Cape Hatteras slope, HS796, Stn11	0–5 cm	22.3	2.6	10.4	12	1.86	1.73
Cape Hatteras slope, S7/KC1	60–68 cm	15.9	2.8	24.6	24.4	0.65	1.62
High Organic Loading							
Eagle Harbor, WA	SWI	42.5	3.5	11.2	11.1	3.83	1.35
Mitchell Bay, WA	SWI	52.2	4.4	7.6	10.9	4.79	1.21
SOILS							
Albia Alfisol Ap, NJ	0–13 cm	13.5	1.2	8.2	11.4	1.18	1.29
Albia Alfisol native A, NJ	0–6 cm	78.0	3.1	3.5	15.04	5.19	1.64
Gumz Mollisol aquic Ap, IN	0–23 cm	79.6	5.5	1.2	15.03	5.30	1.51
Satanta Mollisol ustic Ap, KS	0–12 cm	4.0	0.7	7.8	8.6	0.47	1.24
Richfield Mollisol Ap, KS	0–13 cm	16.2	2.3	41.6	47.6	0.34	1.38
Kibler Ultisol udic Ap, VA	0–20 cm	59.6	3.4	23.6	57.1	1.04	1.53
Howell Ultisol udic Ap, MD	0–13 cm	43.3	3.1	17.3	38.6	1.12	1.41

First column indicates place of origin, sample ID and state in U.S.A. (if applicable). Second column indicates sampling depth in core (SWI = sediment-water interface). Third and fourth columns provide OC concentrations before and after muffling, while fifth and sixth columns indicate surface area before and after muffling. Seventh column provides the organic matter loading at the site, as mg of OC (before muffling) divided by mineral surface area (after muffling). Eighth column provides organic matter density (ρ_{om}).

These pore volumes can be converted to organic matter masses only if one knows the density of the organic matter. Densities of biochemicals typically range from 0.8–1.7 g cm^{-3}. There is little information, however, on the densities of bulk sedimentary or soil organic matter, except for measurements made on processed kerogens (Nawachukwu and Barker, 1985 and references therein). To assess how much organic matter could be associated with these pore volumes, we developed a method for organic matter density determination using high-resolution gas pycnometry on sediments and soils before and after organic matter removal.

2. MATERIAL AND METHODS

Sediments and soils were acquired from archived collections (Table 1). Many sediment samples derived from the collection reported in Mayer (1999), which examined the coverage of the sediment mineral surfaces by organic matter. Small changes in organic carbon concentrations and surface area values between this work and that of Mayer (1999) were found, and likely derive from some combination of subsampling and analytical variation. We focused on sediments and soils that have organic matter loadings of 0.2–1.2 mg-OC m^{-2}, because of their importance in carbon cycling. Samples with higher and lower organic matter loadings were also included for comparison.

Soils were air dried and 2 mm sieved. Preparation of sediments began with washing of the sediments with 10% acetone in water to remove seasalt. The acetone promotes coagulation, with negligible loss of total organic carbon. Samples were then centrifuged (40000 g for 20 min), freeze-dried, and subjected to gas sorption analysis (see below). We tested for subsampling variance by performing this sequence of steps on four subsamples of a well-mixed, composite sediment from the Pemaquid site. Subsequent measurements were performed on the same sample before and after muffling rather than on parallel samples, to decrease subsampling variance. Thus, after pore size analysis of the unmuffled samples, the powders were removed from the gas analysis sample tube, quantitatively transferred to an oven and muffled at 350° overnight. Upon cooling, the samples were transferred back to their gas analysis tubes and reanalyzed for gas sorption isotherms.

We tested for the effect of compression on pore size distribution by submitting one marine sediment (Lowes Cove intertidal) and one silty soil (the C horizon of the Stockbridge Dystric Eutrochrept reported in Mayer and Xing, 2001) to centrifugation (47800 g for 30 min). After centrifugation, the samples were freeze dried and then analyzed for pore size distribution as described below.

Gas sorption analysis was performed on a Quantachrome A-1 Autosorb, by subjecting samples to varying partial pressures of N_2 gas (UHP grade) at 77°K. All solids were initially degassed in a vacuum oven (150°C at 50 $\times$ 10^{-3} torr for overnight) to remove surface-adsorbed water, followed by a minimum of 3 h at 10 $\times$ 10^{-3} torr on the instrument degassing station. Sorption at partial pressures of $<$ 0.3 provides data for BET analysis (Brunauer et al., 1938) whereas sorption at higher partial pressure (0.3–1) provides data with which to interpret pore size distributions from gas condensation. Samples were run in both the adsorption and desorption directions over the entire partial pressure range to gain both of these types of information. Pore size distributions were calculated using the BJH method (Barrett et al., 1951), as implemented in the Autosorb instrumental software, assuming slit-like geometry for the pores (see discussion in Mayer, 1994a). Analyzed size ranges were from ca. 2 to 200 nm—i.e., into pores larger than the 2–50 nm mesopore range into the region of macropores (IUPAC, 1985).

Organic carbon analysis of sediments and soils was performed, after removing calcium carbonate by vapor-phase HCl treatment in a Perkin-Elmer 2400 CHN analyzer.

The absolute density of organic matter in each sample was determined using high resolution pycnometry. Duplicate samples were dried at 100° and weighed into preweighed cups made from heavy-duty aluminum foil, whose volume was predetermined by He gas displacement in a Quantachrome Ultrapycnometer. Then the volume of the soil or sediment sample plus foil cup was determined. Net sample weights and volumes were determined by subtracting foil values from total combined values. The foil cups containing the samples were then muffled at 350° overnight to remove organic matter. After weighing, sample volume was remeasured using the Ultrapycnometer. The absolute density of organic matter was determined from weight and volume changes of each sample before and after muffling. Analytical precision, based on repetitive volume measurements, was less than 1% as a coefficient of variation, while ranges of duplicate organic matter density determinations averaged 10% of their values (in no case was it >27%). Subsampling variability likely explains duplicate sample variances. The method was successfully tested using mixtures of minerals (kaolinite or quartz) with organic materials (casein or dextrose). As a test of whether weight loss was due to organic matter volatilization, we compared the weight losses between the 100° and 350° drying steps with the weight loss predicted by assuming that the measured organic carbon losses represent 1/2 of the weight of the organic matter.

Small angle X-ray scattering (SAXS) provides information on the size distribution of scattering objects, and has been used to probe the microstructure of pore space in geological material (Radlinski and Hinde, 2001). Information about the size distribution of scattering objects (sediment-air interfaces within pores) can be retrieved from the scattering intensity, *I(Q),* measured as a function of the scattering vector, Q: $Q=(4\pi/\lambda)\sin(\varphi/2)$, where φ is the scattering angle and λ is the wavelength of the x-rays. A thin layer of dry sediment was fixed between two sheets of Kapton tape and placed in the X-ray beam. All SAXS measurements were conducted at the UNICAT beam line of the Advanced Photon Source (APS) at Argonne National Laboratory (Argonne, Illinois, USA). The UNICAT ultrasmall-angle X-ray scattering instrument utilizes Bonse-Hart double crystal optics to extend the range of the SAXS down to lower scattering vectors. The measured scattering data set is slit-smeared in the horizontal direction, but was numerically desmeared to recover the standard (pinhole-collimated) small-angle scattering data. Details of the UNICAT system are described by Long et al. (2000).

3. RESULTS

3.1. Analytical Considerations

Pore size distributions can be assessed from either the adsorption or desorption leg of sorption isotherms, which generally differ from each other in a hysteresis mode. Desorption isotherms usually provide more accurate assessments of surface area, assuming slit-shaped pores, as indicated by better agreement with surface area values determined from the BET part of the sorption isotherm. This BET determination uses a wholly different set of assumptions to determine surface area. The agreement between these two different approaches is generally presumed to support use of the desorption leg to infer pore size distributions (Mayer, 1994a). Desorption isotherms of condensed gas from slit-shaped pores should also better follow the predictions of the Kelvin equation, that relates pore openings to partial pressure, than adsorption isotherms for slit-shaped pores (Gregg and Sing 1982). For cylindrical pores the adsorption isotherm may be preferable (Groen et al., 2003). The so-called Tensile Strength Effect (Gregg and Sing, 1982) can lead to an inflation of apparent pore volume at a pore size of ca. 3.8 nm, and was commonly seen in our samples. While this inflation is likely an analytical artifact, it has a negligible effect on the conclusions in this paper, given the results presented below. Further, any error is likely to inflate the estimate of pore volume at smaller pore sizes, which allows a more conservative test of our principal hypothesis. We therefore used the desorption leg data.

Variance in the analysis of pore size distributions was assessed by subsampling freeze-dried Pemaquid sediment in quadruplicate and running each subsample through the entire analytical procedure. The coefficient of variation ranged from 35–38% at 2 nm to 11% at 10 nm and remained below that value for larger pore sizes (data not shown). The range of cumulative pore volumes found among these replicates widened at the larger size end of the range, and was considerably greater than analytical error determined by repeated analysis of the same sample in the same tube. The variance among replicates was thus not due so much to random error of pore volume determination at various pore sizes as to consistent differences among samples. Indeed, the BET surface area, which is measured by a different part of the gas sorption isotherm than the pore size distribution, correlated strongly ($p < 0.05$) with the cumulative pore volumes. This correlation corroborates the inference that variance among samples was due to subsampling heterogeneity.

The sensitivity of surface area or pore size measurements to subsampling derives from the importance of a small mass fraction of sediments or soils—their finest grained minerals—to surface area (Mayer and Rossi, 1982). All analyses reported here, therefore, consist of the same subsample analyzed prior and after muffling, with much care to ensure complete transfer of sample between analysis tubes and the beaker in which muffling was carried out.

Centrifugation had little effect on pore volume distribution throughout the pore size range measured (Fig. 1). The pores are evidently resistant to elimination by the compressive forces employed, and the smaller mesopores in the sediment actually showed a small expansion.

3.2. Cumulative Volume Distributions

An example of the dependence of pore volume and surface area upon pore size (Fig. 2) shows that most pore surface area, but only a minor fraction of pore volume, is associated with smaller mesopores (<10 nm in diameter). The surface area calculated from the pore size distribution in the size range analyzed (6.7 $m^2\ g^{-1}$) is very similar to the surface area measured by the BET analysis of the lower partial pressure range (6.8 $m^2\ g^{-1}$), consistent with earlier results (Mayer, 1994a; 1994b).

The total pore volumes associated with the mesopore to small macropore size range (2–200 nm) ranged from 0.014 to 0.31 $cm^3\ g^{-1}$ (Fig. 3). To provide context, these volumes can account for ca. 3–86% of the volume of the minerals themselves, assuming mineral densities (see below) that we found upon muffling. These mesopore volumes are also generally a minor fraction of bulk sediment or soil pore volumes, which are dominated by much larger pores (e.g., Echeverria et al., 1999).

Muffling showed remarkably little impact on the cumulative pore volume plots of most sediments and some of the soils (Fig. 3). Muffling almost always increased the pore volume, but usually by small fractional amounts. One sediment sample

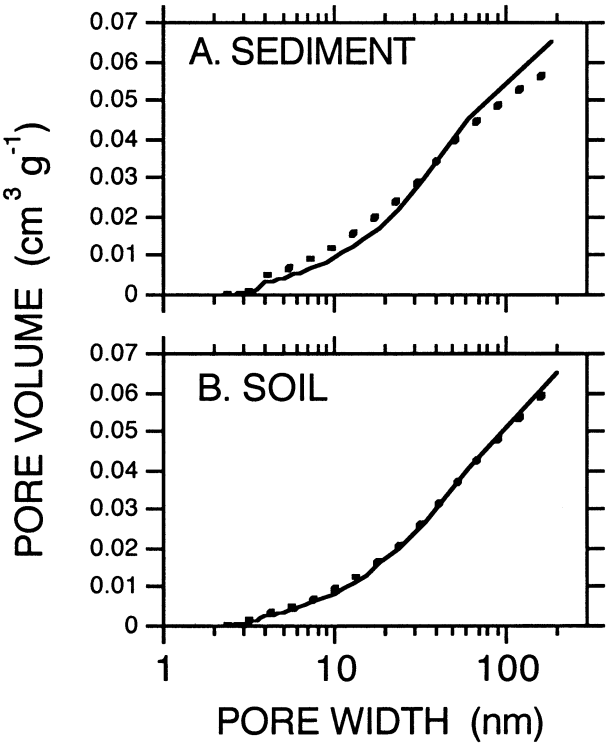

Fig. 1. Effect of centrifugation on pore volume distributions in a marine sediment (Lowes Cove, Maine) and terrestrial soil (Stockbridge Dystric Eutrochrept). Lines represent cumulative pore volumes as a function of pore width. Solid lines are for samples run before centrifugation and dashed lines are after centrifugation.

(Amazon shelf) showed a small consistent decrease in pore volume upon muffling across the entire size range, and several others with essentially no change between unmuffled and muffled treatments showed tiny decreases in pore volume in certain parts of the cumulative curves. Only 1 of 16 sediments and 3 of 7 soil samples showed >50% increases in cumulative pore volume by the 200 nm upper size limit. These generally small relative changes indicate that, for most samples, muffling had minimal impact on the mineral grain geometric relationships that account for pores in this size range. The samples showing the greater increases in pore volume (e.g., Skan Bay among sediments and Gumz Mollisol among soils) generally showed the greatest increases in BET surface area upon muffling, consistent with the importance of mesoporosity to surface area (Fig. 2).

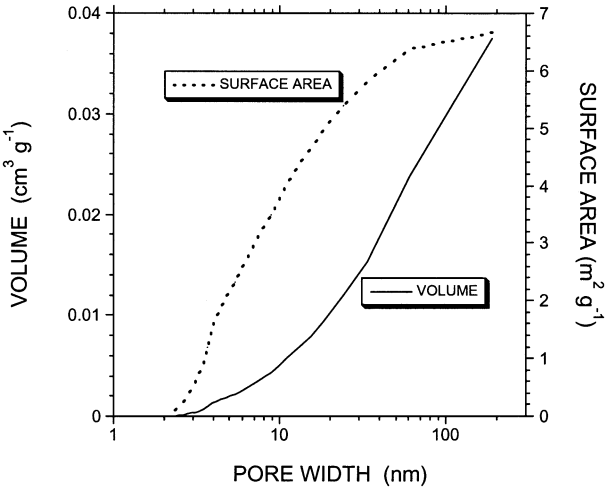

Fig. 2. Cumulative pore volume ($cm^3\ g^{-1}$) and surface area ($m^2\ g^{-1}$) as a function of pore width (nm) for the Lowes Cove sediment.

SAXS data also showed little difference between the unmuffled and muffled Pemaquid and Eel sediments over q values of 10^{-4}–10^{-1} $Å^{-1}$, which correspond to length scales of approximately a few nanometers to a few micrometers (Fig. 4). In a subsequent paper we will discuss in more detail the implications of the SAXS scattering curves, but for now the important finding is that the scattering intensity and dependence on q, which reflect the arrangements of pores and mineral grains, are unchanged between unmuffled and muffled sediments.

3.3. Organic Matter Density

Upon muffling, all samples showed small increases in density—typically 2–14%—to achieve values of 2.4–2.76 g cm^{-3}, which are reasonable values for minerals (Klein and Hurlbut, 1993). Assuming that all of this change was due to oxidation and volatilization of organic matter, then the organic matter density can be calculated according to the differences in weight and volume of the sample between 100° and 350°, or—

$$\rho_{OM} = \Delta\text{weight}/\Delta\text{volume}.$$

As noted earlier, the general agreement between weight loss and the weight loss predicted from OC loss supports use of this formula.

The organic matter densities calculated in this manner range from 1.14–1.86 g cm^{-3} (Table 1). These values are consistent with the range of biopolymeric organic matter densities. Our sedimentary organic matter values are also in the range of kerogen densities determined by more destructive techniques such as mineral dissolution followed by density gradient centrifugation −0.95–2.2 g cm^{-3} (reviewed by Nwachukwu and Barker, 1985). Soil organic matter densities are consistent with the 1.3 g cm^{-3} value determined by Adams (1973) from regressions of bulk density against organic matter content.

4. DISCUSSION

We can combine the organic matter density values with the pore volume determinations to test whether mesopores could hold major fractions of the organic matter content of these soils and sediments. Further, determinations of pore volume before and after muffling allow us to assess the fractions of total organic matter held in pores of various sizes. These calculations rely on whether the density determinations and the change in pore volume are accurate indicators of in situ conditions. Therefore, we first assess potential artifacts in these measures.

4.1. Analytical Considerations

A potential criticism of our use of before-and-after muffling to determine organic matter infilling of mesopores is that the

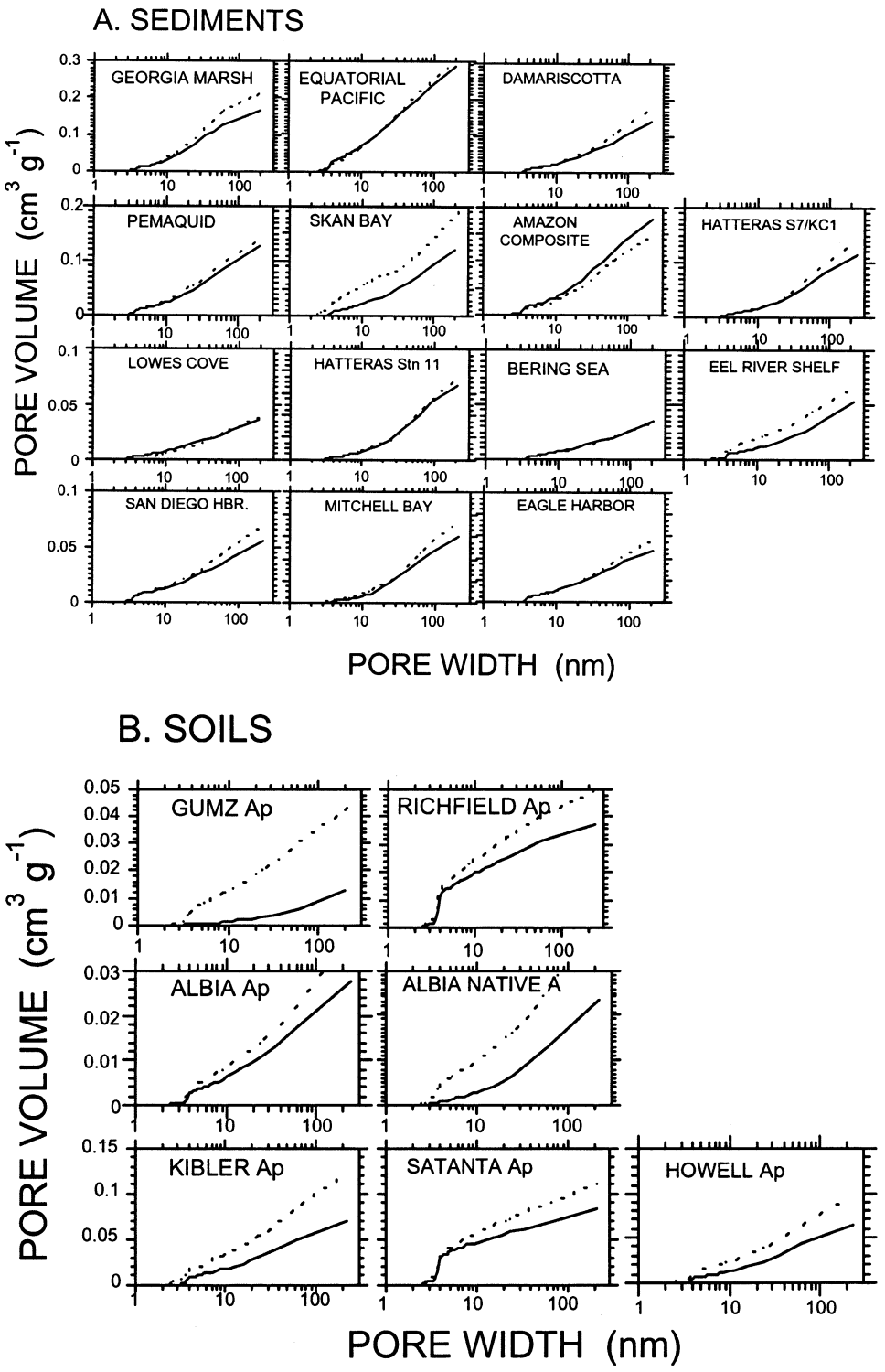

Fig. 3. Cumulative pore volume ($cm^3\ g^{-1}$) in unmuffled (solid line) and muffled (dashed line) sediments (A) and soils (B) as a function of pore width (nm).

muffling process may change the arrangements among phyllosilicate grains that form the pores. We believe that several lines of evidence suggest that these arrangements, collectively called microfabric, remain largely unchanged after muffling. The SAXS data (Fig. 4) indicate that there is no detectable change in the pore structure over 3 orders of magnitude in length scales, suggesting that the microfabric is retained after muffling. Carrado et al. (1997, 2002) also found small changes in pore size distribution by gas sorption measurements upon muffling of synthetic clay-organic matter systems, which they

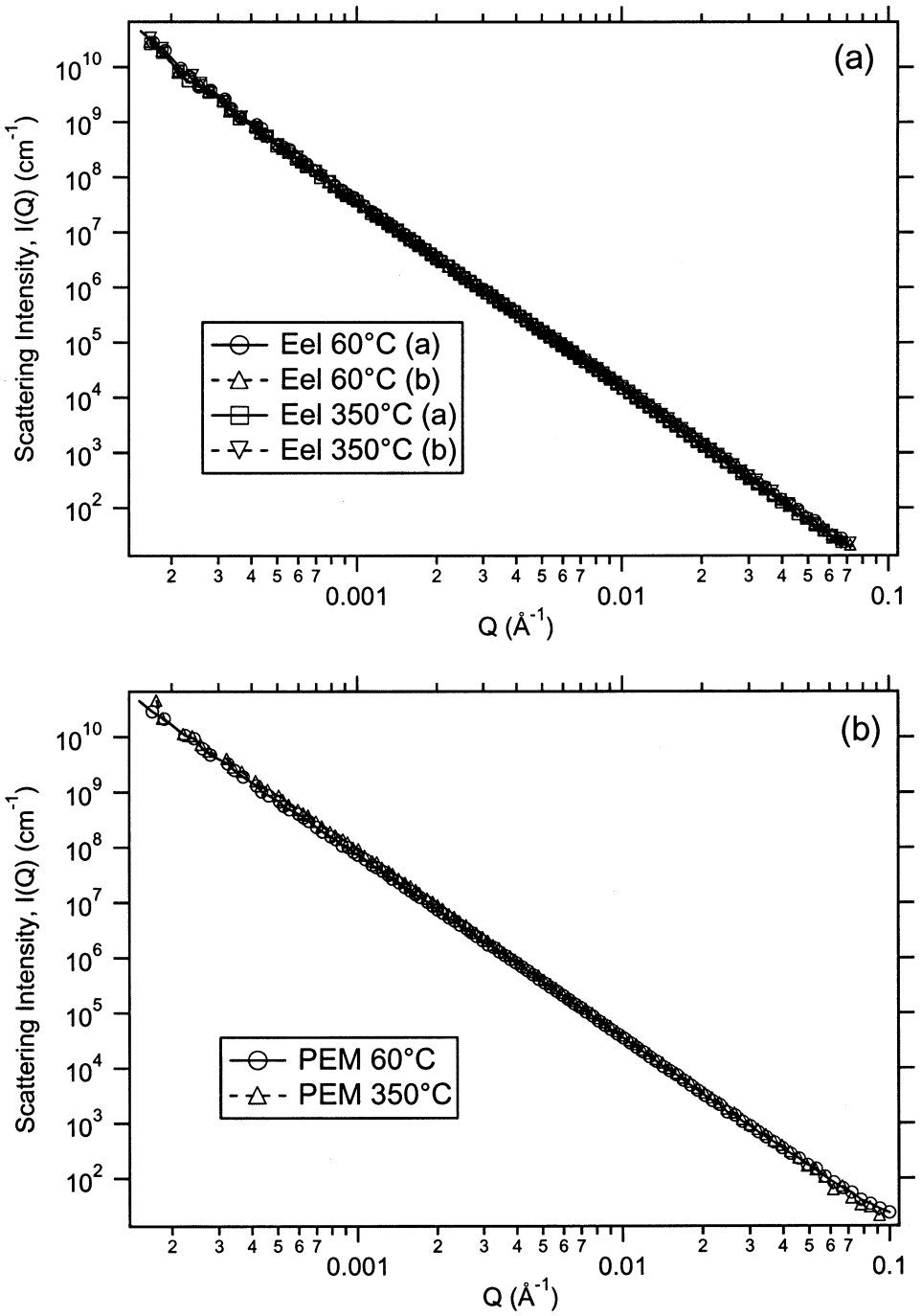

Fig. 4. Small angle X-ray scattering (SAXS) intensities (I) as a function of the scattering vector (Q) for Eel River (a) and Pemaquid (b) sediment samples. Increasing Q corresponds to smaller size. These plots compare scattering intensities for samples that were heated at 60° and 350°, respectively.

corroborated using both SAXS data and TEM observations. They argued that the mesopore size pores are controlled by interparticle contacts among clay tactoids or domains (microaggregates of individual clay crystallites). Indeed, the literature on formation of mesoporous clay catalysts, which relies on using organic templates to create pillared arrangements among clay flakes, routinely uses muffling ("calcination" in that literature) to eliminate the organic templates without loss of mesopore structure (e.g., Zhu et al., 2002). Tolhurst et al. (2002) similarly found no change in card-house microfabric of natural clays upon muffling. Our finding of small impact of centrifugation on pore volume distribution provides further evidence of the robust nature of this microfabric. Last, the deep Pacific clay sample (Fig. 3), which contained very little organic matter, changed its cumulative pore volume by only 0.5% between the unmuffled and muffled treatments. This very small change in

pore size distribution shows that muffling doesn't affect this microfabric in the absence of organic matter.

X-ray diffraction of clays in organoclay aggregates and rocks indicates that individual clay crystallites have c-axis thicknesses of several to tens of nanometers (Eberl et al., 1998; Bock and Mayer, 2000), which is equivalent to several to tens of unit cells. Face-to-face associations between crystallites form to make domains via so-called "turbostratic stacking" (Aylmore and Quirk, 1960; Bennett et al., 1991), and the stacking arrangements among domains can create small, slit-shaped mesopores that result from "bookhouse" or "stepped face-to-face" arrangements (reviewed in Moon, 1972). Frayed edges in crystallites made of several unit cells may create the same kind of porosity. These arrangements are evident in clay microphotographs (e.g., Lee et al., 1991; Hetzel et al., 1994; Dong and Peacor, 1996; Sucha et al., 1996; Mystkowski et al., 2000). Such intercrystallite mesopores apparently hold the majority of surface area of clay-containing sediments and soils, making surface area a sensitive indicator of fine clay content. These arrangements of clay crystallites to form pores and hence surface area, in which the pillars between opposing pore faces are inorganic crystals, probably accounts for the lack of impact of muffling or centrifugation on either pore size distribution or surface area for most samples.

A likely artifact in the organic matter density measurements arises from the larger measured weight losses than those predicted from OC loss. These discrepancies were $<$30% for 14 of the twenty samples measured, and were $>$50% for only 3 of the samples with low OC concentrations. Similar results were found by Ball (1964) using 375^{o} oxidation. The probable cause of these discrepancies is the loss of water from minor amounts of hydrous minerals present in the samples, a problem that becomes negligible for samples with OC contents of greater than several mg g^{-1}. While a correction for this discrepancy might be made by applying a density of 1 (for H_2O) to the extra weight loss, uncertainty about this water density in mineral structures leads us to ignore the potential artifact. Most likely such a correction would lead to increases of no more than several tens of percent in the calculated organic matter densities, which would not materially affect the hypothesis tests addressed in this paper.

The density determinations of organic matter also assume that organic matter density in situ is the same as that following the drying step that precedes the unmuffled density measurement. If in situ organic matter shrinks during the 100^{o} premeasurement drying step—i.e., was expanded like a gel in its in situ state—then our density values are too high. We cannot assess this potential artifact, but we note that it can affect only the volume of organic matter present in pores and not its mass. If the organic matter held in pores was expanded in situ, due to water content that was eliminated by our drying pretreatment, then our calculation of organic matter volume held inside a pore would be off by the degree of expansion. In other words, our determinations of in situ volumes and densities would have errors that cancel in the determination of in situ masses. The mass of organic matter held in pores would not change unless there was a physical movement of organic matter into or out of pores during drying. For our calculation we assume no such movement, and note that our subsequent conclusions depend on the veracity of this untested assumption.

4.2. Pore Filling by Organic Matter

The greatest increases in BET surface area and in pore volume were associated with those samples richest in organic matter, in keeping with the similar finding for surface area by Kahle et al. (2002). This overall relationship implies that pore blockage is due to organic matter, although the blockage may occur because of either pore filling or simple coverage of the pore openings (e.g., Deere et al., 2002).

The potential fractions of a sample's total organic matter held in pores of various sizes are calculated as the mass of organic matter that would fit into the pore volume of the muffled samples, presumably representing the total pore volume between mineral grains once organic matter is removed, and dividing by the total organic matter concentration of the soil or sediment. Thus,

$$\text{Potential fraction} = \rho_{OM} \times PV_w/TOM,$$

where ρ_{OM} is the measured organic matter density, PV_w is the cumulative pore volume at pore width w, and TOM is total sample organic matter (calculated as 2 $\times$ [OC]). Samples for which the unmuffled samples' pore volume values exceeded that of the muffled samples yield negative values and are here presented as zero.

The potential for small mesopores to hold organic matter is considerable (Fig. 5). Ten of 21 samples have sufficient volume by a pore size of 8 nm to hold more than half of their organic matter. All but two samples (the Gumz and Albia Native A soils) have enough mesopore volume to hold more than half of their total organic matter by pore sizes of less than several tens of nanometers.

The fraction actually contained within these pores is calculated as above, but substituting the volume difference between unmuffled and muffled samples at pore width w, presumably representing organic matter volatilized by muffling, for the total pore volume. The Amazon sediment would yield negative values, because of pore volume reduction upon muffling, and in such cases this calculation is therefore meaningless.

The fractions thus calculated to be held in pores of $<$ 8 nm width are usually minor— $<$ 10–20% for most samples. Only one sample, Skan Bay, is an exception, with more than half of its organic matter in pores of $<$ 15nm width. This sample is anomalously high in diatom fragments, as seen by microscope and corroborated by biogenic silica measurements (unpub. data). Diatom frustules are rich in mesopores (Hurd et al., 1981), and organic matter filling of such pores possibly accounts for this sample's anomalous behavior.

The generally small fractions of organic matter calculated to be held in pores of $<$ 8 nm could be explicitly protected by enzyme exclusion, because enzymes are larger than these widths. If the occluded mesopores are not filled with organic matter but rather blocked by adsorption at pore openings (Deere et al., 2002; Kaiser and Guggenberger, 2003), then even these small fractions of organic matter are likely not protected by this exclusion hypothesis.

Only small fractions of surface area in most sediments and soils appear to be coated with organic matter (Mayer, 1999; Mayer and Xing, 2001; Arnarson and Keil, 2001). We have shown here that most organic matter is likewise not contained within smaller mesopores that are formed by the surfaces of

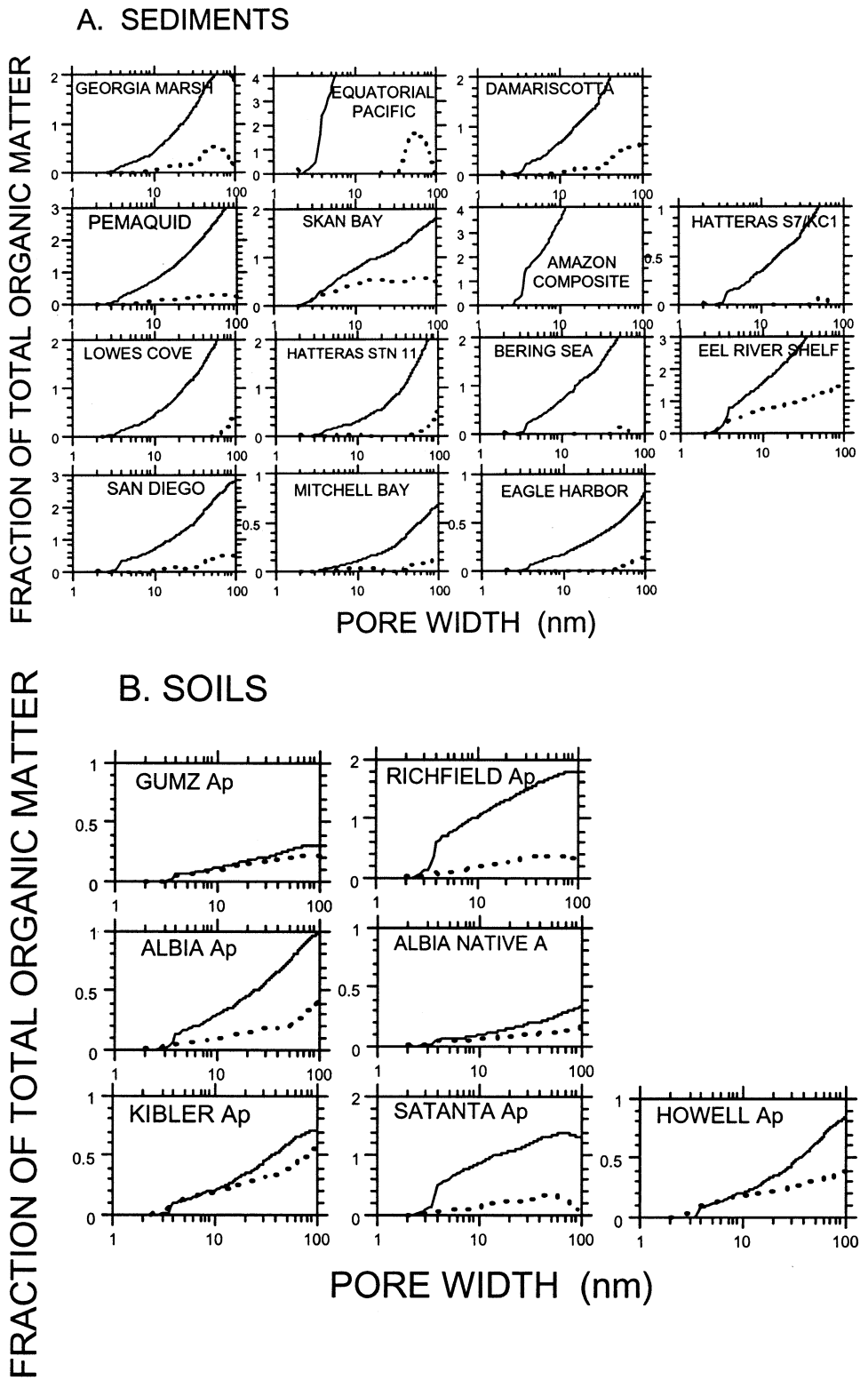

Fig. 5. Cumulative fraction of total OM potentially (solid lines) and actually (dashed lines) held in mesopores as a function of pore size for sediment (A) and soils (B). Due to missing ρ_{OM} values, the Pemaquid ρ_{OM} value was used for the Damariscotta sample and the Skan Bay value was used for the Bering Sea sample.

clays. The "blebs" of organic matter inferred in these earlier papers are largely external to small mesopores.

The question then arises as to why surface area and organic matter are so tightly correlated in soils and sediments if they are not immediately adjacent. The most reasonable answer is that surface area is a marker for clay domains that are physically associated with organic matter. The role of the organic matter seems likely to be that of aggregating agent, one which is physically unconnected with the bulk of surface area, at least at nm distances. The high surface area in this scenario would be incidental.

Chemically, most clay surface area consists of the faces of siliceous tetrahedral sheets. Natural organic matter appears to adsorb preferentially on aluminous clay edges rather than on siliceous faces (Schultess and Huang, 1991; Kubicki et al., 1997), which is corroborated by the finding of Kaiser et al. (2002) that organic matter on surfaces is associated with aluminum and not silicon. This preference is not strongly established and needs more attention. If true, it follows that sorption of organic matter to clay crystallites is not to the faces that account for most surface area and form the walls of most mesopores.

Why, then, might organic matter be physically protected by this form of aggregation, if not contained within pores that can exclude enzymes? One hypothesis is that the network of pores that allow access to organic matter within the aggregates may include "throats" of small mesopore size. These "throats" would be formed by contacts among crystallites or domains. In this scenario, the mesopore exclusion hypothesis may still apply. This hypothesis can be framed in absolute and/or kinetic forms. In the absolute form, there exist pores too small to allow enzyme diffusion to parcels of organic matter held in larger pore spaces. In the kinetic form, the diffusional hindrance caused by some combination of pore size and tortuosity will slow access of digestive agents to organic substrate, and return of solubilized food, that makes it physiologically unprofitable for an organism to make the attempt. Calculations indicate that bacterial success is constrained by a maximum distance between cell surface and food substrate, beyond which exuded hydrolytic enzymes cannot generate a net positive return in terms of nutritional hydrolyzate (Vetter et al., 1998). The tortuosity created by a network of platy minerals may influence this distance, making food resources out of reach. Mechanistic study of physical protection mechanisms in organoclay aggregates may benefit from study of diffusion within these aggregates, which may differ considerably from diffusion through bulk sediment or soil.

5. CONCLUSIONS

We have determined that only minor fractions of organic matter are contained within pores small enough to exclude hydrolytic enzymes, for most of the soils and sediments analyzed. Because many of these samples represent environments with moderate organic matter loadings that dominate organic burial fluxes, we conclude that simple enclosure into these small mesopores cannot explain the lack of degradation of the bulk of organic matter in these environments. Small fractions of organic matter are apparently held in such pores, unless the increases in pore volume observed were due to blocking of openings of mesopores, and these small fractions may be protected by enzyme exclusion. Enzyme exclusion may still be a protective mechanism for the bulk of organic matter, but only via a more complicated microfabric arrangement.

Acknowledgments—We thank D. Thistle, N. Rabalais, R. Aller, S. Henrichs, R. Wheatcroft, S. Naidu, I. Voparil, D. DeMaster, R.F.L. Self, and T. Reinsch (National Soil Survey Center, U.S. Dept. Agric.) for sharing samples of soils and sediments. This research was supported by NSF (Marine Chemistry) and the Donors of the American Chemical Society (Petroleum Research Fund). The UNICAT facility at the Advanced Photon Source (APS) is supported by the U.S. DOE under Award No. DEFG02-91ER45439, through the Frederick Seitz Materials Research Laboratory at the University of Illinois at Urbana-Champaign, the Oak Ridge National Laboratory (U.S. DOE contract DE-AC05-00OR22725 with UT-Battelle LLC), the National Institute of Standards and Technology (U.S. Department of Commerce) and UOP LLC. The APS is supported by the U.S. DOE, Basic Energy Sciences, Office of Science under contract No. W-31-109-ENG-38. Contribution number 387 from the Darling Marine Center.

REFERENCES

Adams W. A. (1973) The effect of organic matter on the bulk and true densities of some uncultivated podzolic soils. *J. Soil Sci.* **24,** 10–17.

Adu J. K. and Oades J. M. (1978) Physical factors influencing decomposition of organic materials in soil aggregates. *Soil Biol. Biochem.* **10,** 109–115.

Arnarson T. and Keil R. G. (2001) Organic-mineral interactions in marine sediments studies using density fractionation and X-ray photoelectron spectroscopy. *Org. Geochem.* **32,** 1401–1415.

Aylmore L. A. G. and Quirk J. P. (1960) Domain or turbostratic structure of clays. *Nature* **167,** 1046–1048.

Ball D. F. (1964) Loss-on-ignition as an estimate of organic matter and organic carbon in non-calcareous soils. *J. Soil Sci.* **15,** 84–92.

Barrett E. G., Joyner L. G., and Halenda P. P. (1951) The determination of pore volume and area distributions in porous substances. I. Computations from nitrogen isotherms *J. Am. Chem. Soc.* **73,** 373–380.

Bennett R. H., O'Brien N. R. and Hulbert M. H. (1991) Determinants of clay and shale microfabric signatures: Processes and mechanisms. In *Microstructure of Fine-Grained Sediments: From Mud to Shale* (eds. R.H. Bennett, W.R. Bryant, M.H.) Hulbert, pp. 5–32. Springer-Verlag, New York.

Brunauer S., Emmett P. H. and Teller E. (1938) Absorption of gases in multimolecular layers. *J. Am. Chem. Soc.* **60,** 309–319.

Carrado K. A. and Xu L. (1997) Materials with controlled mesoporosity derived from synthetic polyvinylpyrrolidone-clay composites. *Micropor. Mesopor. Mat.* **27,** 87–94.

Carrado K. A., Csencsits R., Thiyagarajan P., Seifert S., Macha S. M., and Harwood J. S. (2002) Crystallization and textural porosity of synthetic clay minerals. *J. Mater. Chem.* **12,** 3228–3237.

Deere J., Magner E., Wall J. G., and Hodnett B. K. (2002) Mechanistic and structural features of protein adsorption onto mesoporous silicates. *J. Phys. Chem. B.* **106,** 7340–7347.

Diaz J. F. and Balkus K. J. (1996) Enzyme immobilization in MCM-41 molecular sieve. *J. Mol. Catal. B.* **2,** 115–126.

Dong H. and Peacor D. R. (1996) TEM observations of coherent stacking relations in smectite, I/S and illite of shales: Evidence for MacEwan crystallites and dominance of $2M_1$ polytypism. *Clays Clay Min.* **44,** 257–275.

Eberl D. D., Nüesch R., Sucha V., and Tsipursky S. (1998) Measurement of fundamental illite particle thicknesses by X-ray diffraction using PVP-10 intercalation. *Clays Clay Min.* **46,** 89–97.

Echeverria J. C., Morera M. T., Mazkiaran C, and Garrido J. J. (1999) Characterization of the porous structure of soils: adsorption of nitrogen (77K) and carbon dioxide (273K), and mercury porosimetry. *Eur. J. Soil Sci.* **50,** 497–503.

Furukawa Y. (2000) Energy-filtering transmission electron microscopy (EFTEM) and electron energy-loss spectroscopy (EELS) investiga-

tion of clay-organic matter aggregates in aquatic sediments. *Org. Geochem.* **31,** 735–744.

Gregg S. J. and Sing K. S. W. (1982) Adsorption, Surface Area and Porosity. Academic Press, London, 303 pp.

Groen J. C., Peffer L. A. A., and Perez-Ramirez J. (2003) Pore size determination in modified micro- and mesoporous materials. Pitfalls and limitations in gas adsorption data analysis. *Micropor. Mesopor. Mat.* **60,** 1–17.

Hedges J. I. and Keil R. G. (1995) Sedimentary organic matter preservation: an assessment and speculative synthesis. *Mar. Chem.* **49,** 81–115.

Hedges J. I. and Oades J. M. (1997) Comparative organic geochemistries of soils and marine sediments. *Org. Geochem.* **27,** 319–361.

Hetzel F, Tessier D., Jaunet A.-M., and Doner H. (1994) The microstructure of three Na^+ smectites: The importance of particle geometry on dehydration and rehydration. *Clays Clay Min.* **42,** 242–248.

Hurd D. C., Pankratz S. S., Asper V., Fugate J., and Morrow H. (1981) Changes in the physical and chemical properties of biogenic silica from the Central Equatorial Pacific: Part III, Specific pore volume, mean pore size, and skeletal ultrastructure of acid-cleaned samples. *Am. J. Sci.* **281,** 833–895.

IUPAC. (1985) Reporting physisorption data from gas/solid systems, with special reference to the determination of surface area and porosity. *Pure Appl. Chem.* **57**, 603–619.

Kahle M., Kleber M. and Jahn R. (2002) Carbon storage in loess derived surface soils from Central Germany: Influence of mineral phase variables. *J. Plan Nutr. Soil Sci.* **165,** 141–149.

Kaiser K. and Guggenberger G. (2003) Mineral surfaces and soil organic matter development. *Eur. J. Soil Sci.* **54,** 219–236.

Kaiser K., Eusterhues K., Rumpel C, Guggenberger G. and Kögel-Knabner I. (2002) Stabilization of organic matter by soil minerals—investigations of density and particle-size fractions from two acid forest soils. *J. Plan. Nutr. Soil. Sci.* **165,** 451–459.

Klein C. and Hurlbut C. S. (1993) Handbook of Mineralogy. Wiley, New York, 681 pp.

Kubicki J. D., Itoh M. J., Schroeter L. M. and Apitz S. E. (1997) Bonding mechanisms of salicylic acid adsorbed onto illite clay: An ATR-FTIR and molecular orbital study. *Env. Sci. Tech.* **31,** 1151–1156.

Lee S. Y. Hyder L. K., and Alley P. D. (1991) Microstructural and mineralogical characterization of selected shales in support of nuclear waste repository studies. In *Microstructure of Fine-Grained Sediments: From Mud to Shale* (eds. R.H. Bennett, W.R. Bryant, and M.H. Hulbert), pp. 545–560. Springer-Verlag, New York.

Long G. G., Allen A. J., Ilavsky J., et al. (2000) The Ultra-Small-Angle X-ray Scattering Instrument on UNICAT at the APS, In *SRI99: Eleventh U.S. National Synchrotron Radiation Instrumentation Conference* (eds. P. Pianetta, J. Arthur, and S. Brennan), pp. 183–187. AIP Conference Proceedings CP521, New York: American Institute of Physics.

Mayer L. M. (1994a) Surface area control of organic carbon accumulation in continental shelf sediments. *Geochim. Cosmochim. Acta* **58,** 1271–1284.

Mayer L. M. (1994b) Relationships between mineral surfaces and organic carbon concentrations in soils and sediments. *Chem. Geol.* **114,** 347–363.

Mayer L. M. (1995) Sedimentary organic matter preservation: an assessment and speculative synthesis—a comment. *Mar. Chem.* **49,** 123–126.

Mayer L. M. (1999) Extent of coverage of mineral surfaces by organic matter in marine sediments. *Geochim. Cosmochim. Acta* **63,** 207–215.

Mayer L. M. and Rossi P. M. (1982) Specific surface areas in coastal sediments: Relationships with other textural factors. *Mar. Geol.* **45,** 241–252.

Mayer L. M. and Xing B. (2001) Organic carbon-surface area-clay relationships in acid soils. *Soil Sci. Soc. Am. J.* **65,** 250–258.

Moon C. F. (1972) The microstructure of clay sediments. *Earth-Sci. Rev.* **8,** 303–321.

Mystkowski K., Srodon J. and Elsass F. (2000) Mean thickness and thickness distribution of smectite crystallites. *Clay Min.* **35,** 545–557.

Nwachukwu J. I. and Barker C. (1985) Variations in kerogen densities of sediments from the Orinoco Delta, Venezuela. *Chem. Geol.* **51,** 193–198.

Radlinski A. P. and Hinde A. L. (2001) Applications of small angle neutron and small angle X-ray scattering to petroleum geology. In *Environmental studies using neutrons at synchrotron facilities*, ILL/ESRF, Grenoble.

Ransom B., Bennett R. H., Baerwald R. and Shea K. (1997) TEM study of in situ organic matter on continental margins: occurrence and the "monolayer" hypothesis. *Mar. Geol.* **138,** 1–9.

Ransom B., Kim D., Kastner M. and Wainwright S. (1998) Organic matter preservation on continental slopes: Importance of mineralogy and surface area. *Geochim. Cosmochim. Acta* **62,** 1329–1345.

Schulthess C. P. and Huang C. P. (1991) Humic and fulvic acid adsorption by silicon and aluminum oxide surfaces on clay minerals. *Soil Sci. Soc. Am. J.* **55,** 34–42.

Sollins P., Homann P. and Caldwell B. A. (1996) Stabilization and destabilization of soil organic matter: mechanisms and controls. *Geoderma* **74,** 65–105.

Sucha V., Srodon J., Elsass F. and McHardy W. J. (1996) Particle shape versus coherent scattering domain of illite/smectite: Evidence from HRTEM of Dolna ves clays. *Clays Clay Min.* **44,** 665–671.

Tolhurst T. J., Gust G., Paterson D. M. (2002) The influence of an extracellular polymeric substance (EPS) on cohesive sediment stability. In *Fine Sediment Dynamics in the Marine Environment* (eds. J.C. Winterwerp, C. Kranenburg), pp. 409–425. Elsevier.

Vetter Y. A., Deming J. W., Jumars P. A. and. Krieger-Brockett B. B (1998) A predictive model of bacterial foraging by means of freely released extracellular enzymes. *Microb. Ecol.* **36**, 75–92.

Zhu H. Y., Ding Z., Lu C. Q. and Lu G. Q. (2002) Molecular engineered porous clays using surfactants. *Appl. Clay Sci.* **20,** 165–175.

Zimmerman A. R., Goyne K. W., Chorover J., Komarneni S. and Brantley S. (2004) Mineral mesopore effects on nitrogenous organic matter adsorption. *Org. Geochem.* **35,** 355–375.