Mesodensity organo–clay associations in a near-shore sediment

Michael J. Bock, Lawrence M. Mayer [*]

Darling Marine Center, University of Maine, 193 Clarks Cove Road, Walpole, ME 04573, USA

Abstract

The well-known correlation between mineral grain size and organic matter concentrations in sediments has recently been parameterized in terms of organic matter per unit surface area. Normalized thus, organic matter concentrations in many ocean margin sediments are on the order of 1 mg organic carbon m^{-2} (Mayer, L.M., 1994a. Relationships between mineral surfaces and organic carbon concentrations in soils and sediments. Chem. Geol. 114, 347–363; Mayer, L.M., 1994b. Surface area control of organic carbon accumulation in continental shelf sediments. Geochim. Cosmochim. Acta 58, 1271–1284.). If this organic matter is physically associated with fine clay grains, the resultant organo–clay aggregates should have a density of ca. 2.2 g cm^{-3}, but if associated with larger grains the densities should be much closer to those of pure minerals. We found organo–mineral aggregates of density 2.0–2.3 g cm^{-3} (''mesodensity'') in a shelf sediment to contain the majority of the sedimentary organic matter and surface area. Their mineralogy was composed almost exclusively of fine clays. The correlation of organic matter concentration with sediment surface area may thus be derivative of associations with the fine clay minerals that largely control sediment surface area. Pore size distributions of these aggregates indicate that most surface area is contained within small mesopores of < 10 nm width. Thus, the hypothesis of organic matter protection by enclosure within small mesopores must be framed within the context of inter- rather than intragranular pores. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: organo–clay aggregates; organic matter; sediment; surface area; Gulf of Maine

1. Introduction

Organic matter concentrations have long been known to correlate with mineral grain size. Historically, these correlations were made with classical grain size measures, such as percent clay (Premuzic et al., 1982; Coppedge and Balsam, 1992). Over the past three decades, this association has been parameterized by correlations between organic matter content and sediment specific surface area (Suess, 1973; Tanoue and Handa, 1979; Mayer et al., 1988; Keil et al., 1994; Mayer, 1994a,b; Bergamaschi et al., 1997). Clay size grains contribute to specific surface area much more strongly than their mass contribution (Mayer and Rossi, 1982), so that the clay content and surface area correlations with organic matter may be derivative of one another. Indeed, TEM examination of organic matter in modern sediments

[*] Corresponding author. Tel.: +1-207-563-3146 ext. 237; fax: +1-207-563-3119; e-mail: lmayer@maine.edu

substantiates a strong association between organic matter and clay mineral grains (Ransom et al., 1997).

If normalized to a specific surface area, organic matter concentrations in many ocean margin sediments are in the order of 1 mg organic carbon m^{-2} (Mayer, 1994a,b). If this organic matter is primarily associated with clay sized mineral grains, reduction in the density of the resultant organo–clay aggregations can be expected. For example, clay size fractions yield specific surface areas of ca. 60 m^2 g^{-1} (Mayer and Rossi, 1982; Murray and Quirk, 1990a; Keil et al., 1994). Assuming clay platelets with aspect ratio of 10:10:1, then the average clay crystallite size necessary to provide this surface area is $100 \times 100 \times 10$ nm. Assuming a clay mineral density of 2.5 g cm^{-3}, an organic matter density of 1.0 g cm^{-3} and the 1 mg organic carbon m^{-2} loading, the resultant density of this organo–clay aggregate should be on the order of 2.2 g cm^{-3}. This calculation is independent of the physical nature of the association — that is, fully dispersed adsorbed monolayer vs. more discrete blobs. Organic matter associated with the larger grains, having lower specific surface area, should have densities much closer to a pure mineral density of 2.5–2.65 g cm^{-3}. Organo–clay aggregates with a reduced density should be separable by heavy liquids.

Separation of organo–mineral fractions in marine sediments has historically employed density cutoffs on the order of 1.9 g cm^{-3}, too low a density to separate out the organo–mineral aggregates hypothesized above (Gershanovich and Zaslavskiy, 1983; Prahl and Carpenter, 1983; Ertel and Hedges, 1985; Mayer, 1994a). A more extensive set of studies derives from the soil literature (reviewed by Christensen, 1992), in which greater attention has been paid to intermediate, or ''mesodensity'', density ranges. Organo–clay associations have been found to dominate in these mesodensity separates from soils (Shaymukhavemtov et al., 1984). We thus tested for the presence, nature, and quantitative importance of such mesodensity, organo–clay aggregates in a marine sediment. Our focus has been to assess the fraction of total organic matter held in these mesodensity associations, the nature of the minerals with which they are associated, and relationships between the organic matter and the mineral surfaces. Such a demonstration would extend the conclusions drawn to date from correlational and microscopic evidence of organo–clay associations.

2. Methods

A gravity core was used to sample sediments off of Pemaquid Point, ME (43°49′N, 69°31′W) in December 1989 in 89 m of water. The core was sectioned into 2 cm depth horizons and stored at −20°C. Various depths from this core have been analyzed for organic matter, surface area and ^{14}C dating (Mayer et al., 1993; Mayer, 1994a,b; Mayer, 1995). For density separations, we combined the material from 62–68 cm depth horizons to represent values in deep/old sediments and from the 4–8 cm horizons to represent shallow/recent sediments; whole-sediment ^{14}C ages suggest an age difference of about 1000 years between the shallow and deep horizons (Mayer et al., 1993).

Sediment samples were separated into low and high-density fractions using heavy liquid flotation (Prahl and Carpenter, 1983; Ertel and Hedges, 1985; Mayer et al., 1993; Keil et al., 1994). We used cesium chloride (CsCl) saturated solutions ($\rho = 1.9$ g cm^{-3}) and sodium polytungstate (NaW) solutions ($\rho = 1.9, 2.0,$ and 2.3 g cm^{-3}) to obtain the desired density cutoffs. CsCl has been used extensively in the past but it is limited to a maximum density of 1.9 g cm^{-3}. The monovalent ions of CsCl cause less dissolution of organic matter than the divalent polytungstate anions. NaW is non-toxic and has a wide range of potential densities, up to 3.1 g cm^{-3}.

For all density separations, 5 g of freeze-dried sediment was mixed with 15 ml of heavy liquid solution. The samples were vortex mixed just long enough to suspend the solids (5–10 s). The two density phases were separated by centrifuging at 38 000 RCF (relative centrifugal force) for 30 min. The lower-density material floating above and in the heavy liquid following centrifugation was carefully transferred to a separate tube by glass pipet. This extraction procedure was repeated with fresh solution until no additional material was observed in the fluid phase, at which point one additional heavy liquid separation was performed. The heavy liquid was removed from the density separates by repeated washes with 10:90 acetone:water (v:v, to promote

coagulation) and centrifuging. The samples were then freeze-dried and weighed.

For the 2.3 g cm^{-3} NaW separations in the two depth sections of the core, samples were run both with and without a sonication pretreatment, in order to compare the strength of attachment between the low- and high-density fractions. The sonicated samples were mixed with 2.3 g cm^{-3} NaW solution and sonicated for 15 min, using a Fisher Model 300 with a 4 mm probe at 35% power, prior to performing the separation. With the exception of the addition of the sonication step, the procedure was identical to that described above.

To assess relationships of surface area and mineralogy with mineral particle size fractions, we performed a particle size separation on a sample drawn from the 75 cm horizon of the core. We removed organic matter from the sample using a concentrated sodium hypochlorite treatment at 60°C–80°C. The sediment was washed with 10% acetone/water (v/v) and then made to 0.002% (wt/wt) in sodium pyrophosphate to promote particle dispersion. Particle size separations were then performed by sieving at 63 μm, followed by gravitational and centrifugal separations for the finer size intervals (Folk, 1974). Extraordinary care was taken to ensure complete removal of finer fractions during settlings, repeating the separation procedure until no further turbidity was observed in supernatants. This care entailed up to dozens of iterations over a period of several weeks. The settling-derived size separations were then sieved through a series of Nitex screens (down to the 7 μm cutoff) to ensure particle size, with retentates washed repeatedly on the screen with sodium pyrophosphate solution. The sodium pyrophosphate was then washed off the sediment size fractions and the sediment freeze-dried before weighing, X-ray diffraction, and specific surface area analyses.

Density separates and source material were analyzed for organic carbon and nitrogen on a Perkin Elmer 2400 elemental analyzer. Prior to analysis, the small amount of carbonate material was removed using vapor phase acidification with HCl. The analytical precision was < 5%.

The surface area values, pore size distributions and C-constants of the samples were measured using N$_2$ gas adsorption with a Quantachrome Autosorb-1.

Surface area was calculated using the multi-point BET approach in the normal fashion (Brunauer et al., 1938); analytical precision was 1%. We examined the C-constant in the BET equation to assess the degree of organic matter coverage of mineral surfaces (Mayer, 1999). Briefly, this approach relates the energetics of gas adsorption on surfaces to the relative amounts of exposed mineral vs. organic surface. This method has been validated using a series of model systems. Application of the method requires fastidious measurements of gas adsorption in the low partial pressure range, followed by data editing to use only those points that rigorously obey the BET isotherm. Pore size distributions were calculated from 40-point adsorption/desorption isotherms above a partial pressure of 0.29; the desorption data are presented here.

Mineralogy was determined for both size and density separations by X-ray diffraction, on a Rigaku Miniflex X-ray diffractometer with CuKα radiation and variable slits. While the size separates already had organic matter removed, the density separates from the 2.3 g cm^{-3} NaW separation were treated with sodium hypochlorite to remove their organic matter. Random orientation powder mounts were used to determine phyllosilicate content relative to the tektosilicates. To improve signal:noise in random orientation mounts, we used very slow scans (0.05° min^{-1}). The non-clay mineralogy of these sediments is dominated by quartz, with quartz:feldspar ratios of ca. 16 and < 2% calcium carbonate, so that quartz represents the bulk of the non-clay mineral fraction. We therefore calculated phyllosilicate content according the method of Shultz (1964), using the intensity ratio of the phyllosilicate 020 peak (4.48 Å) to the adjacent quartz 100 peak (4.26 Å). This approach assumes that all phyllosilicates are dioctahedral, which we verified by examination of the phyllosilicate 060 peaks (Moore and Reynolds, 1997). Use of the quartz 100 peak is valid in the absence of authigenic quartz (Eslinger et al., 1973), for which there was no evidence in these samples. We calibrated this method with mixtures of quartz and ground muscovite, which gave similar results as calibration curves with either kaolinite or montmorillonite.

The mineralogy of the clay fraction was determined with more oriented slides to emphasize the

clay 00l peaks, using slurries dried on glass slides. The standard sequence of KCl, $MgCl_2$, HCl and ethylene glycol treatments were applied to distinguish among the various clay minerals (Moore and Reynolds, 1997).

Density separates were analyzed visually under a compound microscope to look for organic detritus, large mineral grains and organo–mineral aggregates. For each separate from the 2.3 g cm^{-3} density cut-off from the deep horizon, about 1 g of material was suspended in 1.5 ml glycerine and examined at $200 \times$. Four fields of view from each sample were photographed and the particles in these photographs were scored as either aggregates or mineral grains. The ratio of aggregates to mineral grains was calcu-

lated and we tested for differences between the two density phases using a chi-squared test. Additional photographs were taken at $400 \times$ to show more clearly the clay aggregates.

Size separates were analyzed by scanning electron microscopy. Dilute suspensions of each separate were placed on double-sided tape, dried, and coated, and examined under a Zeiss DSM940A SEM.

3. Results

3.1. Density separates

For separations at densities of 1.9 and 2.0 g cm^{-3}, there was $< 2\%$ (by mass) in the low-den-

Table 1

Compositional characteristics of the whole sediments and density separates for the shallow and deep horizons given as percentage mass, organic carbon concentration (OC, mg g^{-1}), nitrogen concentration (TN, mg g^{-1}), carbon:nitrogen ratio (C:N, wt/wt), surface area (SFA; m^2 g^{-1}), organic carbon:surface area (OC:SFA; mg m^{-2}), C-constant and % phyllosilicate. The first column details the heavy liquid and density cutoffs used, with $< x$ indicating that the material had a density of less than x g cm^{-3} and $> x$ indicating a density greater than x g cm^{-3}

	% Mass in fraction	OC (mg g^{-1})	TN (mg g^{-1})	C:N	SFA (m^2 g^{-1})	OC:SFA	C-constant	% Phyllosilicate
Shallow								
Whole sediment	–	21.1	2.7	7.8	22.2	0.95	81	57
High density								
> 1.9 (NaW)	98.0	18.7	2.7	7.0	21.4	0.88	106	n.d.
> 2.3 (NaW, unsonicated)	74.7	11.4	1.7	6.8	13.1	0.88	87	52
> 2.3 (NaW, sonicated)	66.9	8.3	1.3	6.5	11.2	0.74	101	53
Low density								
< 1.9 (NaW)	2.0	108	10.9	9.9	–	–	–	n.d.
< 2.3 (NaW, unsonicated)	25.3	46.5	5.7	8.2	49.3	0.9	103	91
< 2.3 (NaW, sonicated)	33.1	44.9	5.4	8.3	50.9	0.9	98	92
Deep								
Whole sediment		18.0	2.6	6.9	22.3	0.81	91	60
High density								
> 1.9 (CsCl)	99.8	17.1	2.5	6.9	18.5	0.92	76	n.d.
> 1.9 (NaW)	99.4	16.0	2.4	6.8	23.1	0.70	100	n.d.
> 2.0 (NaW)	98.1	15.7	2.3	6.9	19.6	0.80	113	n.d.
> 2.3 (NaW, unsonicated)	84.8	11.5	1.7	6.8	15.1	0.76	106	57
> 2.3 (NaW, sonicated)	71.7	6.7	1.2	5.7	12.4	0.54	88	54
> 2.3 (NaW, bleached)	71.0	–	–	–	31.9	–	135	n.d.
Low density								
< 1.9 (CsCl)	0.21	165	15.7	10.5	n.d.	n.d.	n.d.	n.d.
< 1.9 (NaW)	0.63	175	17.7	9.9	n.d.	n.d.	n.d.	n.d.
< 2.0 (NaW)	1.93	71.7	7.9	9.1	40.1	1.8	72	n.d.
< 2.3 (NaW, unsonicated)	15.2	43.8	5.2	8.4	58.3	0.75	97	94
< 2.3 (NaW, sonicated)	29.3	42.1	5.2	8.1	69.9	0.60	99	92
< 2.3 (NaW, bleached)	29.0	–	–	–	96.7	–	136	n.d.

sity fraction (Table 1; Fig. 1), with the shallow horizon having three times that of the deep horizon in the < 1.9 g cm^{-3} fractions. Separations at 2.3 g cm^{-3} removed considerably more material into the low-density fraction. With the sonication pretreatment, the 2.3 g cm^{-3} density solution yielded 29%–33% low-density material from both the shallow and deep core horizons. Because of the negligibly low

yields of < 1.9 and 2.0 g cm^{-3} material, all of this < 2.3 g cm^{-3} separate is assigned to the mesodensity fraction, i.e., material in the 1.9–2.3 g cm^{-3} or 2.0–2.3 g cm^{-3} density ranges. Omitting the sonication step, the < 2.3 g cm^{-3} yield was reduced only a small amount in the shallow horizon but by roughly half in the deep core horizon. This result suggests that the mesodensity material becomes ''glued'' to
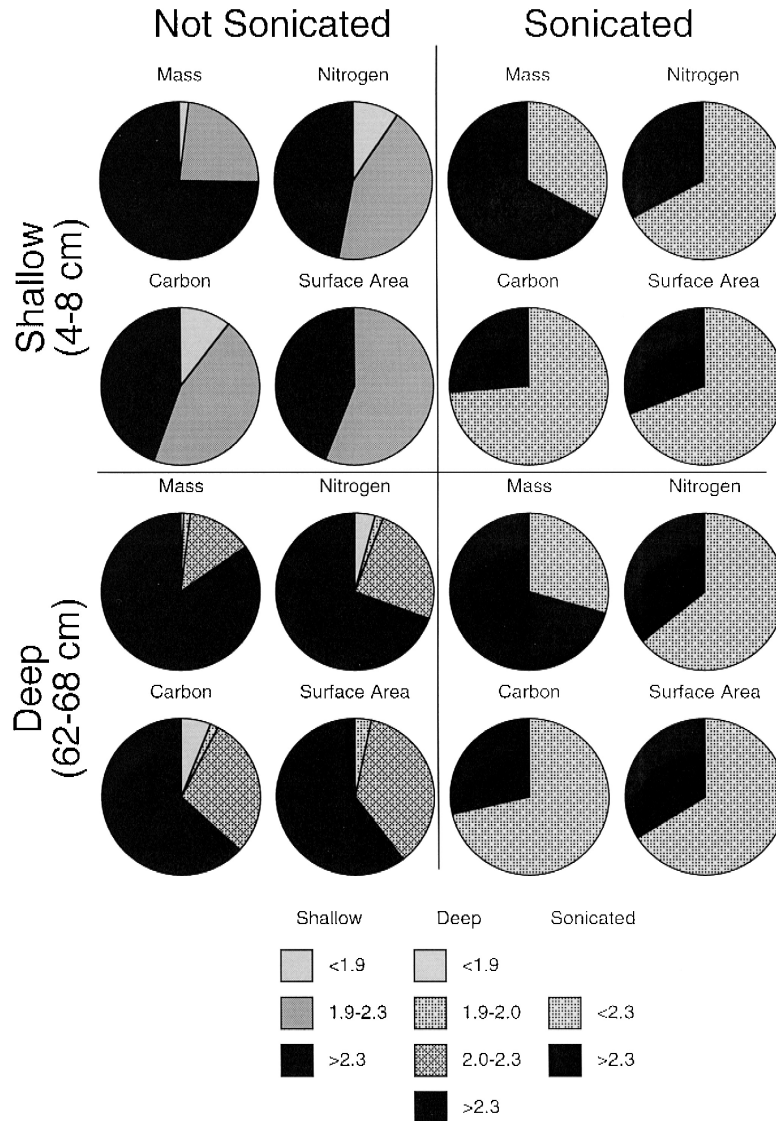

Fig. 1. Proportions of mass, organic carbon, nitrogen and surface area found in the various density ranges. The shallow and deep horizons are separated into sonicated and not sonicated.

larger mineral grains with time following sediment burial. The overall mass recovery efficiency for the density separations was $> 95\%$ (Table 2).

The organic carbon and nitrogen concentrations were much higher in the low-density fractions than in the corresponding high-density fractions (Table 1). The C:N ratios ranged from 5.7 to 10.5, and were always higher in the low-density fractions than the corresponding high-density fractions. Most of the organic matter was found in the < 2.3 g cm^{-3} fractions, except for the unsonicated sample from the deep horizon of the core (Fig. 1). Only minor proportions of the total organic matter were found in fractions with density < 2.0 g cm^{-3}, as was found for this core by Mayer et al. (1993). The recovery efficiencies for organic carbon and nitrogen were usually $> 90\%$ and always above 86% (Table 2).

The specific surface areas of the low-density fractions were also much higher than both the high-density fractions and the source material (Table 1). Insufficient material was recovered for surface area analysis of the < 1.9 g cm^{-3} fractions. Consistent with the organic matter results, 41%–70% of the whole sediment surface area was found in the meso-density fractions.

C-constants from gas adsorption can be used to ascertain the extent of coating of mineral grains by organic matter (Mayer, 1999). The C-constants of the whole sediment and density separates were all similar to one another, within the resolution of this method. The sediment from this core has less than about 15% coverage of the mineral surfaces by organic matter (Mayer, 1999), similar to a wide variety of sediments having monolayer-equivalent concentrations of organic matter from around the world. Thus the mineral surfaces in all density ranges were largely exposed and not covered with organic matter.

Pore size distributions of the various fractions were similar to those reported previously for marine sediments (Mayer, 1994a,b). The shapes of the N_2 adsorption isotherms were consistent with slit-shaped pores, as would be expected from the dominance of platy minerals packed together (Murray and Quirk, 1990b). Data from the desorption leg of the isotherms are presented because their cumulative surface area agrees better with the BET surface area, in accord with the conclusion of Murray and Quirk (1990b). The majority of surface area was associated with small mesopores of less than 10 nm (100 Å) diameter (Fig. 2). The high-density fraction appears to have a somewhat greater fraction of its surface area associated with particularly small pores of less than 4 nm diameter (Fig. 2).

The mineralogy of the mesodensity fraction was more than 90% phyllosilicate, as indicated by the peak height ratios of the dioctahedral clay 020 peak to the adjacent quartz 100 peak. These phyllosilicates consisted of 10 Å illite/mica, Fe-rich chlorite, vermiculite and kaolinite. There were relatively minor decreases in the percent phyllosilicate between the source material and the high-density fraction, indicating mass loss of phyllosilicates of less than 10% upon density separation. The bulk of phyllosilicate in the source rock is therefore in the form of relatively coarse grained minerals (e.g., metamorphic mica grains — see below) with significant mass but not surface area. The mass loss of phyllosilicate from the source material was not sufficient to account for the appearance of inorganic mass in the low-density fractions. This discrepancy is likely due to a combination of factors, such as poorer crystallinity of the fine-grained clays (relative to larger phyllosilicates, yielding lower, mass-specific diffraction intensities) and perhaps other materials in the low-density fraction. For example, a broad rise in diffractogram in the $20°$–$30°$ 2θ region implies biogenic silica in the low-density fractions (Moore and Reynolds, 1997).

Table 2

Recovery budgets of material in the density separates calculated as the percent of the material in the source material recovered in the high and low-density separates. The first column details the heavy liquid and density cutoff used

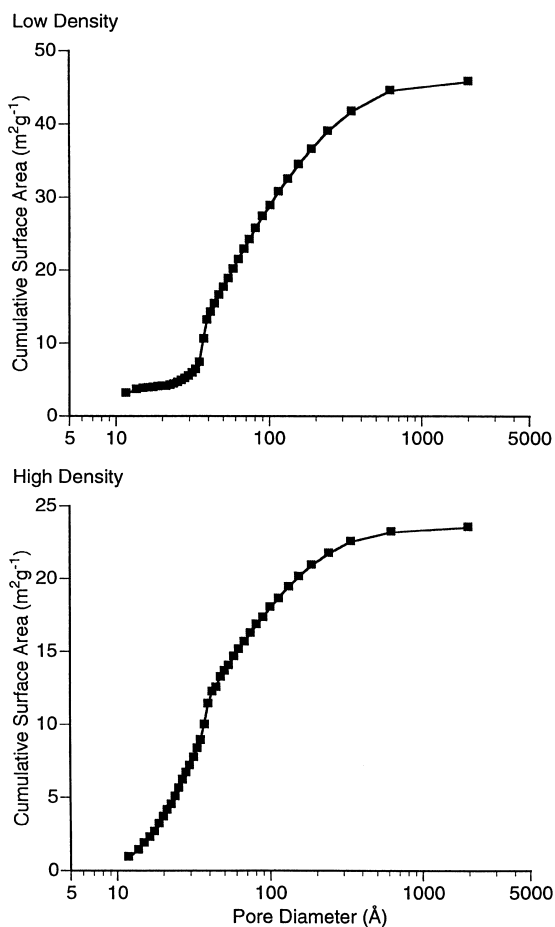|	Treatment	% Mass	% C	% N	% SFA
Shallow	NaW 1.9	95.4	94.8	100.8	88.4
	NaW 2.3	95.5	113.9	111.3	93.7
	NaW 2.3 (sonicated)	95.5	94.0	93.7	103.9
Deep	CsCl 1.9	97.2	92.6	93.6	79.7
	NaW 1.9	98.8	91.7	93.2	99.8
	NaW 2.0	98.8	92.1	89.8	83.4
	NaW 2.3	101.4	94.8	86.5	85.7
	NaW 2.3 (sonicated)	94.6	90.6	86.2	109.2

Fig. 2. Cumulative BET surface area ($m^2 \, g^{-1}$) vs. pore diameter (Å) for the shallow sediment horizon separated using 2.3 g cm^{-3} NaW. The y-axis shows the cumulative surface area contained in pores smaller than the x-axis value.

Microscopic examination of the samples revealed that the high- and low-density fractions at the 2.3 g cm^{-3} cutoff contain similar components, but in different proportions. In both density ranges, distinct grains and aggregates can be seen (Fig. 3, photos at $400\times$). The aggregates usually had a brownish color — presumably deriving from organic matter. The two density fractions had different proportions of distinct grains and aggregates. To quantify this difference, we captured four fields of view at $200\times$ and counted the numbers of distinct grains vs. aggregates. The ratios of aggregates to distinct grains were 0.94:1 for the low-density fraction and 0.06:1

for the high-density fraction, and significantly different ($p < 0.001$, chi-square test). Clearly, the low-density fraction had many times the number of aggregates found in the high-density fraction. However, the ratio of distinct grains to aggregates does not take into account the sizes and shapes of the particles and therefore should not be used to infer the relative masses or volumes of the two particle types.

3.2. Size separates

The mass distribution among the size separates indicates that the sediments can be characterized as a silty clay, with about half of the mass in the $< 2 \, \mu m$ fraction (Table 3). X-ray diffraction data indicate that virtually all of the material in the $< 2 \, \mu m$ fraction was phyllosilicate, consisting of illite/mica, Fe-rich chlorite, and minor amounts of kaolinite and vermiculite. Diffractograms for these phyllosilicates were identical to those of the mesodensity fraction discussed above. Crystallite thicknesses in the 00l direction, as indicated by peak widths at half-maximum, were on the order of 20–30 unit cells for most of these clays. However, these thicknesses are weight-averaged, and do not preclude significant amounts of clay platelets that are much thinner and, hence, more important in creating surface area. Similar phyllosilicate peaks were observed in coarser fractions, though narrower peaks indicated thicker crystallites.

Specific surface area values in the size separations of the sample pretreated to remove organic matter revealed a dramatic rise only in the $< 2 \, \mu m$ fraction (Table 3). The specific surface area in the $< 2 \, \mu m$ fraction was 56.6 $m^2 \, g^{-1}$, which is similar to the values in the low-density fraction obtained using 2.3 g cm^{-3} NaW. The surface area values found in the $> 2 \, \mu m$ fractions are markedly lower than have been reported previously (e.g., Mayer and Rossi, 1982). They are thus closer to the geometrically predicted surface area values based on smooth grain faces — i.e., they have lower roughness coefficients, in keeping with the predictions of Ransom et al. (1998). We believe that these different findings are due to the exhaustive removal of fine-grained contaminants from each size fraction. SEM observations corroborated this lack of clay-sized ($< 2 \, \mu m$) contaminants in the silt size ranges. There was clearly
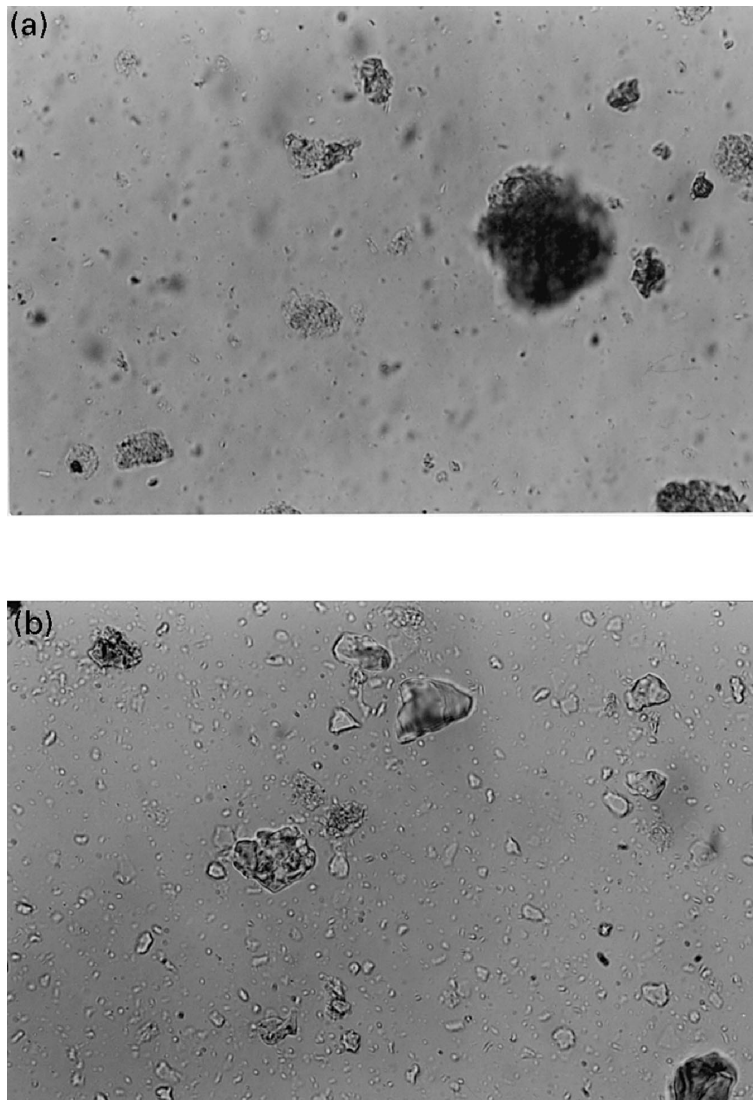
Fig. 3. Photographs of the (a) < 2.3 and (b) > 2.3 g cm^{-3} density separates from the shallow core mounted in glycerine and shown at $400 \times$.

phyllosilicate present in the finer silt fractions, with X-ray diffraction data indicating that the 2–7 μm fraction contained almost half of its mass as phyllosilicates. However, SEM examination of this fraction showed that these phyllosilicate grains were much larger than those found in the < 2 μm fraction, consistent with the crystallite thicknesses calculated from X-ray diffraction peak widths, and would thus provide much less surface area. The exhaustive

separation of clay-sized grains from silt and sand fractions is of course impossible without pretreatment to remove organic matter. Our data thus differ from the surface area-grain size trend found by Keil et al. (1994), whose experimental objectives precluded removal of organic matter before SPLITT separations. The important result from our size separations is that the clay-size fraction (< 2 μm), which is composed almost entirely of phyllosilicates, ac-

Table 3
Distribution of grain sizes separated from the 75 cm horizon of the sediment, along with specific surface areas of grain size separates and results of SEM observations

Size range (μm)	SFA (m^2)
< 2	56.6
2–7	6.2
7–15	3.5
15–20	3.6
20–44	2.3
44–63	1
> 63	3.6

counts for 92% of the overall surface area of the whole sediment.

4. Discussion

In this sediment, significant fractions of mass are present at densities clearly below those of pure minerals (Fig. 1). The low densities of this fraction are presumably due to the association of high-surface area clay minerals with organic matter. These meso-density organo–clay aggregates may result from simple adsorption of organic matter to the clay minerals. However, organic matter (equal to two times the organic carbon concentrations) constitutes 8%–14% of the weight of these aggregates and, hence, 20%–35% of the solid volume of the aggregates (assuming organic matter density of 1 g cm^{-3}). The organo–clay association may thus derive instead from an aggregation reaction.

These organo–clay aggregates contain the major fraction of the sedimentary organic matter (Fig. 1). Based on the similarity in organic carbon:surface area ratios and C-constants between the low- and high-density fractions, the organic matter in the high-density fraction may also be contained in organo–clay aggregates which are, in turn, tightly associated with larger tektosilicate mineral grains. In fact, microscopic examination reveals that some aggregates remain in the high-density fraction (Fig. 3). However, the distinctly lower C:N ratios of the high-density organic matter implies differences in the nature of the organic ''glue'' found in the high- and low-density fractions. The differing nature of the organic matter may have been responsible for the

difficulty in separating some fraction of the organo–clay aggregates from the high-density fraction.

The empirical association between organic matter content and clay-sized (i.e., < 2 μm) mineral content has been known for many years (Premuzic et al., 1982; Coppedge and Balsam, 1992; Keil et al., 1994). This correlation is shown here to have a causal basis, based on our isolation of essentially pure organo–clay aggregates. Preliminary data indicate similar a similar relationship in sediment from another region. Our data are thus in agreement with the TEM observations of Ransom et al. (1997), indicating organic matter to be associated with fine-grained phyllosilicates.

The correlations with sediment specific surface area that provide so much explanatory value for organic matter loadings in continental shelf sediments (e.g., Keil et al., 1994; Mayer, 1994a), may thus be derivative of the clay mineral association. Specific surface area is a sensitive measure of the fine-grained phyllosilicate content (Mayer and Rossi, 1982; Ransom et al., 1998). It has been shown elsewhere (Mayer, 1999) that the monolayer-equivalent loadings of organic matter — ca. 1 mg OC m^{-2} — do not imply full coatings of mineral surfaces. Instead, sediments with these monolayer-equivalent loadings have typically < 15% of their surfaces actually covered with organic matter. Combining the results of that work and this one indicates that much, if not most, sedimentary organic matter occurs as organo–clay aggregates with only a small fraction of the clay surfaces covered with organic matter, in agreement with the conclusions of Ransom et al. (1998).

The spatial distribution of organic matter concentrations in the ocean can be expected to respond to the sedimentological characteristics of organo–clay aggregates. Factors controlling the size of these aggregates will strongly influence their Stokes Law behavior, because of the dependence of settling velocity on the square of particle size. Keil et al. (1994) found significant levels of OC and surface area in the clay through fine silt (ca. 15–20 μm) ranges in hydrodynamic (SPLITT) size separations. Organo–clay aggregates like those found here, containing < 2 μm clay grains, may well account for significant fractions of the organic matter found in their silt size fractions, as suggested by Ransom et

al. (1998). If so, then these aggregates likely have considerable stability, under the hydrodynamic stresses provided by the SPLITT approach, at least up through the 15–20 μm size range.

The lower density of the mesodensity organo–clay aggregates (2.0–2.3 g cm^{-3}) will also affect Stokes Law behavior. However, the excess density of the aggregates over that of the fluid medium is decreased only by 10%–33% relative to the excess density of pure mineral grains, and excess density has only a first-order influence on settling velocity. Thus, the impact of density on settling characteristics of fine clay grains and, hence, surface area, will not be as significant as that deriving from the several-fold change in size (relative to non-aggregated clay grains). However, the prediction of organic matter settling characteristics will be influenced strongly by the clay association, as this association causes major increases in the excess density of organic matter relative to the fluid medium.

Protection of organic matter against biological decay at the monolayer-equivalent level has been hypothesized to be due to its physical location inside pores too small to allow access by the hydrolytic enzymes used by all organisms (Mayer, 1994a,b). The surface area–organic matter–clay association, coupled with the relatively smooth-faced grains implied by low roughness coefficients, implies that the pores associated with organic matter consist of inter-particle, slit-like spaces between clay grains, and not intraparticle dissolution features on minerals (Mayer, 1994b). Hence, this protection hypothesis, if valid, likely works in the context of intergranular rather than intragranular pores. As stated previously (Mayer, 1994a,b), the validity of this preservation hypothesis depends on the position of organic matter relative to the pore geometry — is access to organic matter restricted by intergranular channels available to protein enzymes? The dominance of small mesopores of less than 10 nm diameter in both low- and high-density separates implies that most channels between clay grains are of a size too small to allow penetration by such enzymes.

5. Conclusions

In a near-shore sediment, we found that the majority of the organic matter was present as organo–clay aggregates with densities of 2.0–2.3 g cm^{-3}. Our results provide a mass-based corroboration of the TEM-based observations of Ransom et al. (1997). The classical correlations between organic matter and clay fractions are seen here to be based on a distinct association between major fractions of the sedimentary organic matter and very fine phyllosilicates, whose sedimentological and biogeochemical fates are therefore closely intertwined. The high volume fraction of organic matter in these aggregates, and the low fraction of mineral surface area covered by organic matter, imply that formation of these aggregates should be conceived using aggregation and gluing concepts rather than those of adsorption reactions. The nanometer-scale architecture of these aggregates may play a critical role in the long-term preservation of organic matter.

Acknowledgements

References

Bergamaschi, B.A. et al., 1997. The effect of grain size and surface area on organic matter, lignin and carbohydrate concentration, and molecular compositions in Peru Margin sediments. Geochim. Cosmochim. Acta 61, 1247–1260.

Brunauer, S., Emmett, P.H., Teller, E., 1938. Adsorption of gases in multimolecular layers. J. Am. Chem. Soc. 60, 309–319.

Christensen, B.T., 1992. Physical fractionation of soil and organic matter in primary particle size and density separates. Advances in Soil Science 20, 1–90.

Coppedge, M.L., Balsam, W.L., 1992. Organic carbon distribution in the North Atlantic Ocean during the last glacial maximum. Mar. Geol. 105, 37–50.

Ertel, J.R., Hedges, J.I., 1985. Sources of sedimentary humic substances: vascular plant debris. Geochim. Cosmochim. Acta 49, 2097–2107.

Eslinger, E., Mayer, L.M., Durst, J., Hower, J., Savin, S., 1973. An X-ray technique for distinguishing between the detrital and secondary quartz in the fine-grained fraction of sedimentary rocks. J. Sediment. Petrol. 43, 540–543.

Folk, R.L., 1974. Petrology of Sedimentary Rocks. Hemphill, Austin, TX, 182 pp.

Gershanovich, D.Y., Zaslavskiy, Y.N., 1983. Geochemical characterization of the organic matter in bottom sediments in the upwelling zone in the southeast Pacific. Geochem. Int. 20, 88–96.

Keil, R.G., Tsamakis, E., Fuh, C.B., Giddings, J.C., Hedges, J.I., 1994. Mineralogical and textural controls on the organic composition of coastal marine sediments: hydrodynamic separation using SPLITT-fractionation. Geochim. Cosmochim. Acta 58, 879–893.

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

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

Mayer, L.M., 1995. Sedimentary organic matter preservation: an assessment and speculative synthesis — a comment. Mar. Chem. 49, 2–3.

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., Rossi, P.M., 1982. Specific surface areas in coastal sediments: relationships with other textural factors. Mar. Geol. 45, 241–252.

Mayer, L.M., Macko, S.A., Cammen, L., 1988. Provenance, concentrations and nature of sedimentary organic nitrogen in the Gulf of Maine. Mar. Chem. 25, 291–304.

Mayer, L.M., Jumars, P.A., Taghon, G.L., Macko, S.A., Trumbore, S., 1993. Low-density particles as potential nitrogenous foods for benthos. J. Mar. Res. 51, 373–389.

Moore, D.M., Reynolds, R.C., 1997. X-ray Diffraction and the Identification and Analysis of Clay Minerals. Oxford, New York, 378 pp.

Murray, R.S., Quirk, J.P., 1990a. Intrinsic failure and cracking of clay. Soil Sci. Soc. Am. J. 54, 1179–1184.

Murray, R.S., Quirk, J.P., 1990b. Surface area of clays. Langmuir 6, 122–124.

Prahl, F.G., Carpenter, R., 1983. Polycyclic aromatic hydrocarbon (PAH)-phase associations in Washington coastal sediments. Geochim. Cosmochim. Acta 47, 1013–1023.

Premuzic, E.T., Benkovitz, C.M., Gaffney, J.S., Walsh, J.W., 1982. The nature and distribution of organic matter in the surface sediments of world oceans and seas. Org. Geochem. 4, 63–77.

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

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

Shaymukhavemtov, M.S., Titova, N.A., Travnikova, L.S., Labenets, Y.M., 1984. Use of physical fractionation methods to characterize soil organic matter. Soviet Soil Sci. 8, 131–141.

Shultz, L.G., 1964. Quantitative interpretation of mineralogical composition from X-ray and chemical data for the Pierre Shale. US Geol. Surv. Prof. Paper 391-C, US Gov. Printing Office, WA.

Suess, E., 1973. Interaction of organic compounds with calcium carbonate: II. Organo–carbonate associations in recent sediments. Geochim. Cosmochim. Acta 37, 2435–2447.

Tanoue, E., Handa, N., 1979. Differential sorption of organic matter by various sized sediment particles in recent sediment from the Bering Sea. J. Oceanogr. Soc. Jpn. 35, 199–208.