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Extent of coverage of mineral surfaces by organic matter in marine sediments

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Abstract—Organic matter loading in continental margin sediments frequently occurs at a concentration equivalent to a monolayer coating of mineral grains, raising the question of whether adsorbed organic matter is indeed dispersed over all mineral surfaces. A method was developed to address this configurational issue using the energetics of gas adsorption on oxide surfaces. Enthalpies of gas adsorption were assessed using the C constant of the Brunauer-Emmett-Teller (BET) equation. Physisorption of nitrogen or argon gas involves higher enthalpies onto naked than onto organically coated oxide surfaces. Studies on model adsorbate-adsorbent systems provided an algorithm relating gas adsorption energetics to the fraction of surface coated with organic matter. Application of this algorithm to marine aluminosilicate sediments shows that those with low to moderate loadings of organic matter ($<3 \text{ mg organic carbon m}^{-2}$) have generally less than 15% of their surfaces coated. Most minerals in these sediments, which account for most sediments in the ocean, therefore present a largely naked aluminosilicate surface to aqueous solutions. Copyright © 1999 Elsevier Science Ltd

1. INTRODUCTION

Organic matter in most marine sediments seems to be primarily associated with the mineral phase, as evidenced by an inability to separate the two phases by physical means (Mayer 1994a). A direct proportionality between organic matter concentration and sediment specific surface area (e.g., Mayer 1994a) also suggests a surface association; e.g., adsorption. The physical and chemical nature of this association, however, is poorly known, as is its genesis. The proportionality of organic matter to mineral surface area often has a slope of ca. 1 mg-OC m^{-2} , which is equivalent to the concentration to be expected if a monolayer of moderately-sized organic molecules was evenly spread over all mineral surfaces (Weiler and Mills, 1965; Suess, 1973; Tanoue and Handa, 1979; Mayer 1994a,b; Keil et al., 1994). The manner in which organic matter is associated with mineral surfaces has important implications for understanding of its preservation during burial, its interaction with contaminants, gluing of mineral grains, and other sedimentary problems.

An important first step in the characterization of the organic matter–mineral relationship is simply the assessment of what proportions of mineral surfaces are covered with organic matter. Most techniques for the study of organic films (Perry and Somorjai, 1994) work well with large and flat surfaces such as semiconductors, but have difficulty with finely divided powders or those which have rough surfaces; e.g., sedimentary minerals. Direct microscopy is a promising direction, and has been performed using visible and electron approaches (Foster, 1985; Watling, 1988; Bishop et al., 1992; Ransom et al., 1997). Each approach has the potential to detect organic matter in thicker layers. However, visible light microscopy clearly lacks the resolution to detect organic monolayers, and such detection is also at the limit of electron microscopic technology. No microscopic approach has yet explicitly ruled out thin monolayers on mineral grains because of lack of demonstration that such layers could have been detected had they been present.

Gas adsorption can provide information on both extent and nature of surfaces. Its use has been primarily for the determi-

nation of surface area and pore size distribution. However, the Brunauer-Emmett-Teller (BET: Brunauer et al., 1938) theory for surface area determination contains a term that addresses the energetics of gas adsorption onto the surface. This term, called the C constant, is related to the enthalpy of gas adsorption onto a surface by the expression

$$C = M \exp((\Delta H_{ads} - \Delta H_{cond})/RT) = M \exp(\Delta H_{xs}/RT) \quad (1)$$

where M is a pre-exponential term, ΔH_{ads} is the adsorption enthalpy of the gas directly on the surface, ΔH_{cond} is the enthalpy of gas condensation, normally considered equivalent to adsorption of the second and higher layers of gas (Steele, 1974), ΔH_{xs} is their difference, R is the universal gas constant, and T is degrees Kelvin. M is the nondimensional ratio $(A_1/A)(\nu/\nu_1)$, where A_1 and ν_1 are, respectively, the probability of contact and vibrational frequency of gas molecules in the first layer and A and ν are those of additional gas layers. The ratio M is indeterminate for most adsorbent-adsorbate systems, and is usually considered to equal 1 (Gregg and Sing, 1982).

Relatively high C constants have long been observed for oxide surfaces, and low ones for organic materials (e.g., Lowen and Broge, 1961; Boki et al., 1993). These differences may relate to various factors, such as stronger interaction of slightly quadrupolar N_2 molecules with a heteropolar ionic surface such as an oxide (Barrer, 1966) than with less polar organic material. Organic coatings have been observed to lower the C constant of oxides (Lowen and Broge, 1961; Ahsan, 1992), but this observation has not been exploited to measure coating extent.

This paper evaluates the use of C constants from BET data to assess organic matter coverage of sedimentary mineral grains. The principal question asked with this approach is if monolayer-equivalent levels of organic matter in sediments indeed represent a dispersed coating of organic matter adsorbed over all mineral surfaces, or if the association is more localized. The experimental method is first validated using well defined organic molecules adsorbed on model adsorbents with similar surface chemistry as that of sedimentary minerals. An algorithm is developed to relate C constant information to the

Table 1. Marine sediments used for determination of surface coverage in this study. Surface area values are those determined after hydrogen peroxide oxidation, except for the two Boston Harbor sediments which were oxidized by 350° muffling and the Alaskan coastal peat sample which was measured without oxidation.

Location	Sample notes	Organic carbon (mg g ⁻¹)	Surface area (m ² g ⁻¹)
Amazon shelf core 4221—1	Composite of several core depths	6.3	37.2
Equatorial Pacific	SWI	7.8	94.7
Peru margin	15–16 cm horizon	131.6	23.6
Linekin Bay, Maine coast	3–3 cm horizon	49.9	37.2
Damariscotta estuary, Maine coast	Stn. 7, SWI	23.5	35.3
Lowes Cove, Maine coast	SWI	10.9	6.6
Pemaquid, Maine coast	7/96 core, 14–36 cm composite	20.3	31.3
Miller Island, Maine coast	SWI	27.2	22.9
Boston Harbor, MassPort site*	SWI	71.7	15.4
Boston Harbor, Ft. Independence*	SWI	28.1	3.7
San Diego Harbor, California, Stn. SS 1,2	Composite of two samples, SWI	15.2	17.0
California Shelf, off Eel River	Composite of several samples, sieved	10.2	11.7
Mississippi Delta Sample D2	SWI	6.9	22.2
Huanghe Delta Sample T5	SWI	5.5	22.7
Huanghe Delta Sample D3	SWI	3.6	15.8
Cape Hatteras slope HS797, Stn. 11	SWI	24.7	8.0
Bering Sea shelf, Stn. KS22	SWI	4.8	6.0
Skan Bay, Alaska	2–4 cm horizon	95.8	17.8
Skan Bay, Alaska	10–12 cm horizon	44.3	19.1
Georgia Coastal Marsh	SWI	53.4	48.9
Denmark shelf	SWI	16.0	22.5
Alaska coastal peat**	SWI	175	3.2

SWI = Sediment-water Interface.

* Surface area values are on muffled rather than peroxide-treated samples.

** Surface area value on unoxidized sample.

fractional coverage of oxide surfaces. The application of this algorithm to marine sediments requires development of an oxidation method to examine the naked mineral surface chemistry of any given sediment sample. A series of natural sediments, with varying organic matter loading, is then examined with this approach.

2. METHODS AND MATERIALS

Solids of two types were used in this study; model substrates on which adsorption and other experiments were carried out, and a series of marine sediments on which organic matter coverage was determined. Model substrates used as adsorbents in experimental work included several simple and complex oxides: α -alumina (Alta-Aesar 14558), silica gel (60 Å pore size: Sigma 9258), controlled pore glass (CPG, Inc.), illite (Wards), albite and kaolinite (J. T. Baker, Wards). Marine sediments, selected to represent a wide range of organic matter loadings, were contributed by a number of colleagues, and their origins are described in Table 1. Sediments were stored freeze-dried in a freezer since receipt.

A series of adsorption experiments provided varying organic matter coverage on the different model substrates, and were used to calibrate organic coverage vs. C constant. Adsorbates included cetyl pyridinium bromide (CPB: Sigma), a series of homologous fatty acids (C₃, C₈, C₁₂, C₁₈: Sigma), and adipic acid (Aldrich). All of these compounds were used as received. Most adsorption experiments were conducted from aqueous solutions, with the exception of fatty acids on alumina, for which adsorption was performed from cyclohexane (Kipling and Wright, 1963, 1964). Extent of adsorption was determined by determination of residual adsorbate left in solution (CPB, using UV spectroscopy; see Mayer and Rossi, 1982) and/or organic carbon analysis of the adsorbent after the experiment (CPB, adipic acid, fatty acids). The latter was carried out using standard procedures with a Perkin-Elmer 2400 analyzer.

Natural organic matter on sediments was removed to assess the C constant of the naked minerals. Several forms of oxidation were tried.

First, a combined H₂O₂–0.1 M Na₄P₂O₇ solution (Sequi and Aringhieri, 1977) was added to 1–1.5 g sediment, allowed to sit for 2h. The temperature was slowly raised to 80°, and as liquid evaporated 5 mL aliquots of H₂O₂ were added over the next 1–2 days until frothing stopped (except for samples with high manganese dioxide content, which can cause bubbling indefinitely via catalytic decomposition of the H₂O₂). A second method was oxidation by solutions of NaOCl (13% Cl₂ equivalent) in water (neutralized to pH 9–9.5), which was conducted at 60°–80° for 6h. The third method was by low temperature plasma oxidation (Anton Paar CPA-1), in which sediment is placed in a quartz cell, containing a stir bar, and subjected to a microwave generated, oxygen plasma at 150° for varying periods of time. Periods of 24 h–48 h were necessary to remove the bulk of the organic matter by this method, depending on the sediment. The fourth method was oven oxidation at 350° for 12 h (Keil et al., 1997).

Preparation of sediments for C constant analysis, in the absence of oxidative removal of natural organic matter, began with washing of the sediments with 10% acetone in water to remove seasalt. This wash caused insignificant loss of total organic carbon, and only rarely was any color seen in the wash solutions. Subsequent centrifugation (40,000 RCF for 20 min) and freeze-drying were carried out under the same conditions as aliquots of sediment subjected to oxidative attack.

Gas adsorption analysis was performed on a Quantachrome Autosorb, by subjecting solids to varying partial pressures of N₂ or Ar gas at 77°K. The gases were UHP grade. All solids were initially degassed in a vacuum oven (150°C at 50 × 10⁻³ torr for 18 h) to remove surface adsorbed water, followed by a minimum of 3 h at 10 × 10⁻³ torr on the instrument degassing station. Gas adsorption was performed according to standard techniques except for two factors necessary to achieve the greater accuracy and precision needed for the C constant analyses described here. First, relatively large amounts of solid adsorbent, at least 4 m², were required, in contrast to the normal 1 m² required for accurate surface area analysis. Second, longer gas equilibration times and more stringent tolerances for target adsorption extents also gave improved results. Normal runs comprised ten partial pressures over the range 0–0.3. Data reduction was performed with the BET equation implemented in a spreadsheet rather than the instrumental software, as

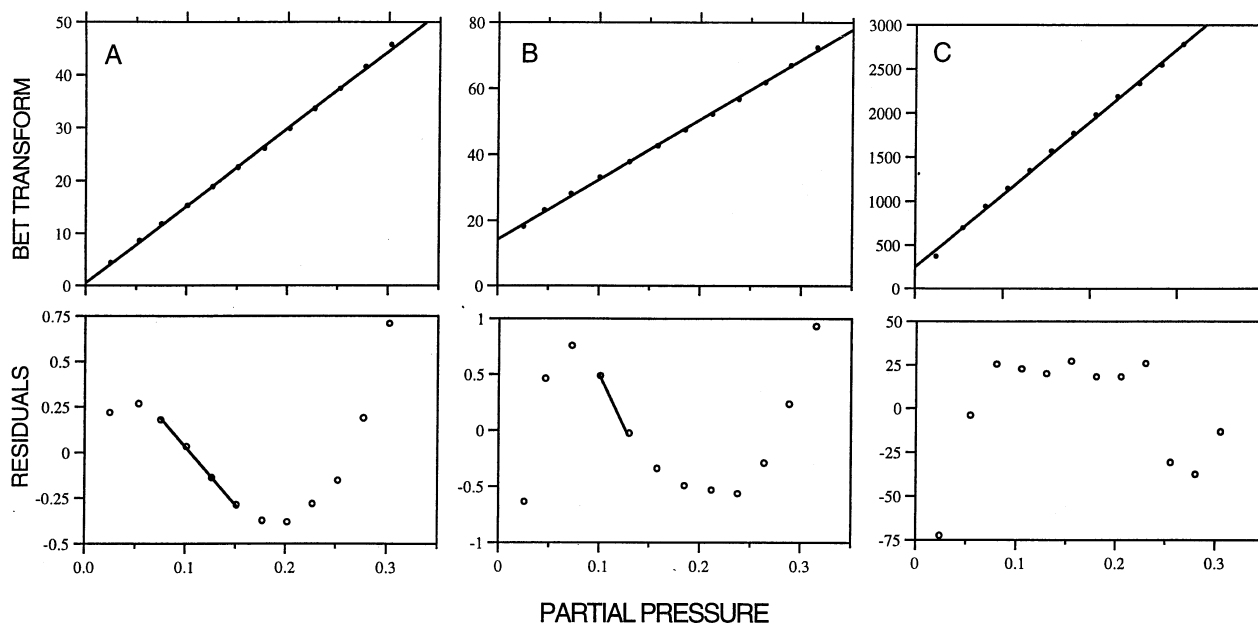


Fig. 1. Data treatment. BET plots (top) and plots of residuals from regression lines (below) versus partial pressure, for N_2 adsorption. The BET transform (y-axis) equals $[(p/p^0)/(0.0012492(1-(p/p^0))V_{ads})]$, where p/p^0 is the partial pressure and V_{ads} is the amount of gas adsorbed. (A) Shelf sediment from Denmark, unoxidized (SFA = $24 \text{ m}^2\text{g}^{-1}$, C constant = 307 without data filtering and 126 using the 0.07–0.15 data points). This sample illustrates a moderately clear linear midsection, and shows improvement from an unreasonable C constant without editing to a reasonable one with editing. (B) Alumina fully coated with stearic acid (SFA = $19.3 \text{ m}^2\text{g}^{-1}$, C constant = 14 without data filtering and 11 with the 0.10 and 0.13 points). This sample shows continuous change in slope at intermediate partial pressures and the manner in which I selected data on such plots. (C) Glutamine (SFA = $0.4 \text{ m}^2\text{g}^{-1}$, C constant = 34 without data filtering). This sample shows the poor residuals plots obtained with very low surface area samples such as organic materials.

the former allowed iterations based on error analysis of results. The analytical precision for ΔH_{xs} values, expressed as a standard deviation calculated from pooled duplicate analyses, is about 0.15 kJ mol^{-1} .

Organic carbon analysis of sediments was performed by first removing calcium carbonate by vapor-phase HCl treatment, followed by analysis in a Perkin-Elmer 2400 CHN analyzer. Precision (as standard error) is typically 1%.

3. RESULTS AND DISCUSSION

3.1. Determination of Reasonable C Constants

For materials of geochemical relevance, the BET equation normally provides an excellent description of gas adsorption onto solids, as shown by highly linear fits of the BET transform (Fig. 1). Although the excellent correlations suffice for highly accurate surface area determination, I found consistent patterns in the residuals to these BET regressions (Fig. 1). These residuals usually show an N-shaped pattern (Fig. 1a,b), with a downward bending of the regression line at very low partial gas pressures (<0.05 – 0.10), an upward bending at the upper end of the partial pressure range (typically >0.2 – 0.25), and a more linear fit to the BET transform in the mid-range of partial pressures, typically 0.08 – 0.20 . The mid-range partial pressure region is generally where monolayer coverage of the surface by gas is reached, depending on the energetics of the gas adsorption (Lowell and Shields, 1984). Qualitatively similar patterns of BET transform shape are evident in the data of Whalen (1967) for N_2 adsorption on silica.

The C constant is calculated from the slope (s) and y-axis intercept (i) at zero partial pressure of a BET plot according to:

$$C = s/i + 1 \cong s/i. \quad (2)$$

The latter approximation results from the typical condition that $s/i \gg 1$. The presence of i in the denominator of this expression causes the C constant to be sensitive to its value. Surface area determination from the isotherm is not similarly dependent on the intercept. Because the intercept is calculated as an extrapolation from the isotherm data, and is very close to the origin, its value can change markedly with small deviations of the data from linearity. In other words, the surface area determination is not significantly affected by small nonlinearities, but the C constant can be strongly affected by them.

The bending of the BET plots at both low and high pressure ends of the spectrum each raise the C constant if the entire data set is used for its calculation. As a result, C constants sometimes reach extremely high values that are energetically impossible given the nature of nitrogen gas sorption on solids. In some cases the bending is sufficient to place the intercept below the origin, yielding a negative C constant which implies the clearly incorrect conclusion of endothermic adsorption of N_2 . However, use of only the data from the linear midsection of the isotherm for calculation of C constants (Fig. 1) was found to give consistent and reasonable values (see below), with no negative intercepts.

The midsections of the BET plots are not linear for all samples. There is sometimes a continuous curvature in the

Table 2. Endmember BET surface area, BET C constant, and ΔH_{xs} values for various oxide and organic substrates analyzed in this study.

	Surface area ($\text{m}^2 \text{g}^{-1}$)	C Constant	ΔH_{xs} (kJ mol^{-1})
OXIDES			
Kaolinite	9–22	49–93	9.6–11.2
Illite	63	123	11.9
Albite	9.0	69	10.5
α -Alumina	14.3	75–109	10.7–11.6
Silica gel (60 Å)	306	114	11.7
Controlled pore glass	16	99–104	11.4–11.5
ORGANIC SOLIDS			
Glutamine	0.4	34	8.7
Tannic acid	0.3–1.0	31–57	8.5–10.0
Adipic acid	0.8	25–50	8.0–9.7

transition between the low pressure downward limb and the high pressure upward limb (Fig. 1b). In these cases, data points that represent the greatest slope on the residuals plot were used. This choice, in the absence of further study, is somewhat arbitrary, but is in keeping with the partial pressure range normally observed with the majority of samples that do have clearly linear mid-sections. Pure organic compound samples (Fig. 1c) don't provide these N-shaped patterns, perhaps because of greater data variance associated with low surface area values.

Clean oxide phases have higher C constants than pure organic materials (Table 2). Using equation (1) to convert C constants to excess enthalpies of adsorption (ΔH_{xs}), these values are consistent with energetics measured by calorimetry on similar materials (e.g., Rouquérol et al., 1979). This agreement substantiates the assumption of $M \approx 1$ (Eqn. 1) for our system. For both oxides and organic materials there are ranges in enthalpy of up to about 2 kJ mol^{-1} ; nevertheless there remain clear differences between oxides and organic compounds. Among oxides, kaolinite frequently yielded low C constants, in keeping with previous observations of low surface energy for this mineral (Boudreau and Cooper, 1987).

A considerable literature has grown over the past several decades, attempting to assess the distribution of site adsorption energies by gas adsorption and other means (Rudzinski and Everett, 1992). The present work does not address this vexing problem. Determination of the entire site energy distribution of gas adsorption onto solids would involve all partial pressures less than ca. 0.3, and the BET approach would be an inappropriate model (Adamson, 1976). In the approach proposed here, adsorption energies are averaged over a restricted part of the adsorption isotherms, and hence the energy calculated via the C constant approach applies only to the ΔH_{xs} values derived from this part of the isotherm (Dormant and Adamson, 1972). The highest energy segment of the site distribution is excluded. This exclusion, as shown below, still allows an internally consistent approach that allows for the main objective, the assessment of surface coverage by organic materials on oxide (e.g., mineral) surfaces, to be met.

3.2. Relationship Between Organic Coatings and ΔH_{xs} : Model Systems

This section addresses the energetics of gas adsorption onto model systems in which organic compounds are adsorbed onto

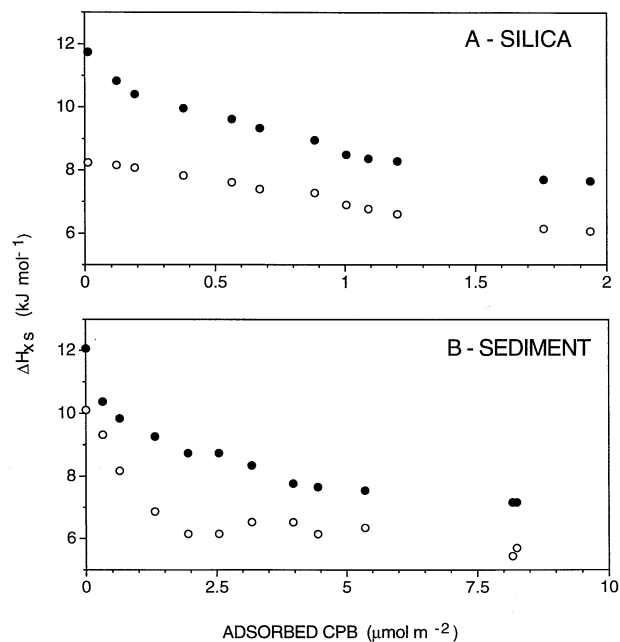


Fig. 2. ΔH_{xs} of N_2 (closed circles) and argon (open circles) adsorption onto (a) silica gel and (b) oxidized marine sediment containing varying levels of preadsorbed CPB.

clean oxide phases representative of those dominating surface chemistry in aluminosilicate sediments. The objectives are to establish the similarity of gas adsorption energetics between organic matter adsorbed onto solids and pure organic materials and to develop an algorithm relating fractional coverage of oxides and ΔH_{xs} values.

Are gas adsorption energetics similar between pure organic phases and oxides fully covered with organic compounds? A useful adsorbate for this test is the cationic surfactant cetyl pyridinium bromide (CPB) used in the determination of surface area in sediments and soils (Greenland and Quirk, 1964; Mayer and Rossi, 1982). The success of this surfactant in surface area measurement is due to its demonstrated ability to fully coat surfaces. Varying amounts of CPB adsorbed onto silica and oxidized marine sediment show a progressive lowering of ΔH_{xs} with increasing CPB coverage (Figure 2). Pretreatment of the sediment with dithionite to remove iron oxides made no difference to the results. A similar decreasing trend in ΔH_{xs} was obtained for an experiment using CPB and kaolinite (data not shown). Thus organic matter adsorbs initially to sites that have higher adsorption enthalpies for gases.

These drops in ΔH_{xs} were not due simply to the physical presence of organic matter. In a separate experiment, a large amount of low surface area organic matter (tannic acid, which has a low C constant) was added to pure kaolinite and physically mixed with it to test if organic matter in physically discrete form would cause a drop in ΔH_{xs} similar to the adsorption experiments. No water was added so that the added tannic acid did not dissolve and then coat the kaolinite. The resultant ΔH_{xs} , with N_2 adsorption, was 10.5 kJ mol^{-1} , essentially the same as that of the naked kaolinite used in this experiment, demonstrating that the drop observed in the CPB

experiments was due to adsorptive cover of the kaolinite surfaces.

The ΔH_{xs} values with N_2 adsorption of the fully coated silica and marine sediment, as determined by plateaus in the adsorption isotherms (not shown), were 7.6 kJ mol^{-1} and 7.2 kJ mol^{-1} , respectively. These values are somewhat lower than, but similar to, those obtained on pure organic materials (Table 2), providing confidence that a mineral surface with a complete organic matter coating will yield ΔH_{xs} values similar to a pure organic material. The lower values of the coated oxides are perhaps more accurate than those found for the pure organic solids, because of the greater accuracy of C constant determination with organically coated solids having much higher surface areas.

Using argon gas instead of N_2 also yielded decreases in adsorption energies upon adsorption of CPB, though the progression of the decreases varied between the two gases for some samples. Argon's ΔH_{xs} values are generally lower by 10%–30% (Fig. 2). These lower values are consistent with argon's lack of quadrupole moment, leading to a less intense interaction with the surface. Enthalpic differences between the two gases were sometimes greater for the naked oxide (Fig. 2a). This difference likely results from highly polar sites on the oxide surfaces exhibiting stronger interactions with N_2 , which has a small quadrupolar moment, during the initial stage of gas adsorption. This narrowing of difference in ΔH_{xs} between N_2 and Ar with increased organic coating is analogous to a similar decrease in differential enthalpy between these two gases observed during progressive adsorption by the gases themselves (Furlong et al., 1980), which can also be interpreted as being due to initial preferential adsorption of gases on highly polar sites. If elimination of surface-quadrupole interactions were the principal basis for changing ΔH_{xs} upon organic coating, then argon should not have shown a decrease in ΔH_{xs} with progressive adsorption of CPB. Instead, other sources of changing ΔH_{xs} are implied, such as topography at the angstrom scale or other ion-multipole interactions between the surface and the gas molecules (Furlong et al., 1980; Steele, 1974).

Experiments such as those reported in Figure 2 provide confidence that a continuous function of decreasing ΔH_{xs} values will accompany the progressive coating of mineral surfaces by organic matter. They do not, however, provide a means to convert ΔH_{xs} to fractional cover, because the manner in which surfactant molecules such as CPB coat the surface is not immediately apparent. In other words, what is the fractional coverage of the inorganic surfaces at various adsorbed surfactant concentrations?

Surfactants are thought to adsorb at low coverages as isolated molecules in various orientations. At higher concentrations they coalesce to form islands of vertically oriented chains and eventually full coatings in this vertical orientation (Scamehorn et al., 1982; Leimbach et al., 1995). The manner in which CPB orients its C_{16} chain, at low coverages and under the gas adsorption conditions of 77 K and vacuum, is not known. The two possibilities relevant to gas adsorption energetics are that the C_{16} chain lies down flat or extends away from the surface. The next experiments therefore examined systems in which the orientation of adsorbed molecules at low coverages could be more accurately assessed and then used to infer the orientation of CPB molecules. Focus was placed on low fractional cover-

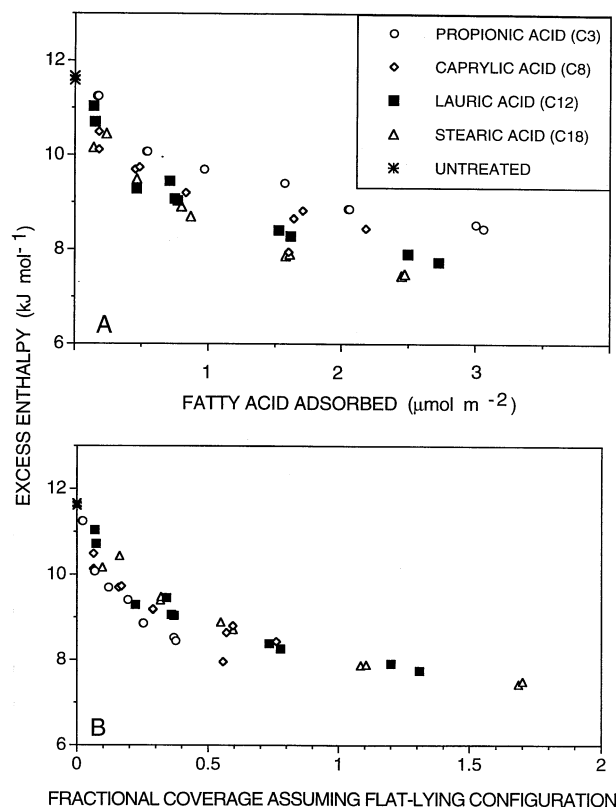


Fig. 3. ΔH_{xs} of N_2 adsorption onto alumina coated with increasing amounts of various adsorbed fatty acids: (a) expressed as molar amount per m^2 adsorbed, and (b) expressed as fractional coverage of entire surface assuming flat lying configuration, except for propionic acid for which only the carboxylate cross section was considered, with cross sectional areas for propionic, caprylic, lauric, and stearic acids of 20.5, 58, 80, and 114 \AA^2 , respectively (Zullig and Morse, 1988; Kipling and Wright, 1963). Fractional coverages exceed 1.0, which is impossible because of the assumption of flat lying configuration. At some point the fatty acids will point away from the surface and the calculation loses accuracy.

ages because, as discussed below, sediments with monolayer equivalent concentrations of organic matter were suspected to have low surface coverages by natural organic matter and it is therefore this part of the spectrum that needed attention to answer the question posed for the study.

To assess the tendency for hydrocarbon chains either to lie flat or extend away from the surface, several homologous fatty acids were adsorbed onto alumina. This approach attaches the carboxylate end of the molecule to surface aluminum atoms, and then tests if larger fatty acids cause progressively greater drops in ΔH_{xs} with increasing hydrocarbon chain length at any given molar coverage of the surface. The data do show greater decrease in ΔH_{xs} with longer chain length at fixed molar adsorption densities (Fig. 3a), consistent with a flat lying configuration. The adsorption densities can be replotted as fractional coverage assuming nonoverlapping, flat-lying molecules with the appropriate, cylindrical, cross sectional areas (Fig. 3b). Thus plotted, the data collapse into a more similar trend of decreasing ΔH_{xs} with increasing adsorptive coverage. This coalescence is strong evidence for flat-lying configuration of hydrocarbon chains under the BET experimental conditions.

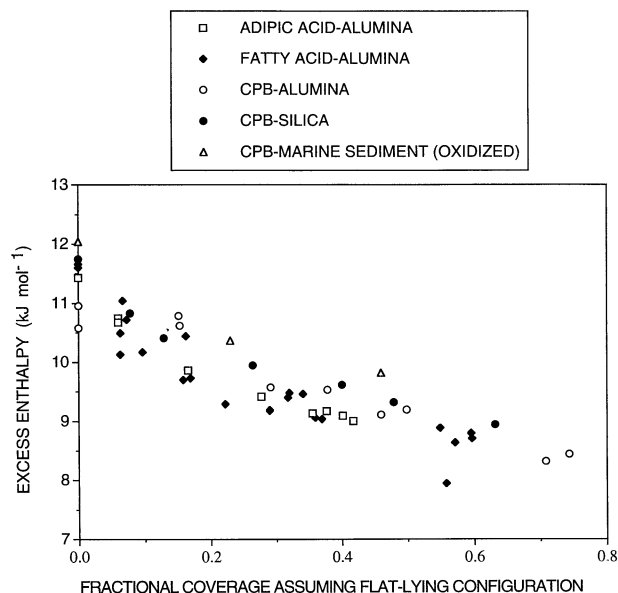


Fig. 4. ΔH_{xs} of N_2 adsorption onto various organic adsorbates coating various adsorbents, including adipic acid and fatty (caprylic, lauric, and stearic) acids on alumina, and CPB on oxidized marine sediment, silica, and alumina. For clarity, the other fatty acid-alumina data (Fig. 4b) are not included here. Cross-sectional areas and consequent fractional coverages calculated using areas assumed above, with CPB assumed to be 120.3 \AA^2 (Slade et al., 1978) and adipic acid to be 47.9 \AA^2 (Wright, 1966)

However, this assumption should not be carried to extensive coverages of the surface ($>0.5?$), because of the likelihood of formation of islands of surfactant molecules in admicelles, with hydrocarbon chains extending away from the surface. The results from these fatty acid alumina experiments imply that CPB, with its C16 group, also lies flat at low surface coverages.

The assumption that aliphatic chains lie flat at low coverages under the vacuum conditions of BET analysis leads to similar relationships between fractional coverage and ΔH_{xs} for all of the adsorbents and adsorbates examined (Fig. 4). At any particular fractional coverage, the ΔH_{xs} values range generally less than 1 kJ mol^{-1} for fractional coverages <1 . Also included in this plot is an experiment with adipic acid adsorbed on alumina. Adipic acid $[(\text{COOH})(\text{CH}_2)_4(\text{COOH})]$ attaches to surface aluminum atoms via each of its terminal carboxyl groups. The molecule can thus be considered a staple on the surface, allowing unambiguous conversion of amount adsorbed to fractional coverage of the surface (Wright, 1966). Its data fit in with the other systems that have hydrocarbon chains. The naked alumina from the CPB alumina experiment shows a low ΔH_{xs} value which is inconsistent with both other runs of this material and the partially coated samples of the same experiment, and is shown here but subsequently disregarded.

The results in Fig. 4 allow derivation of a broadly applicable algorithm relating the fractional coverage of oxide surfaces to the difference in ΔH_{xs} between the naked oxides and those variably coated with organic compounds. This difference ($\Delta(\Delta H_{xs})_{\text{naked-coated solids}}$) is calculated here for nitrogen gas adsorption at 77K. The fractional coverages are calculated for each adsorbent-adsorbate system using the product of the ap-

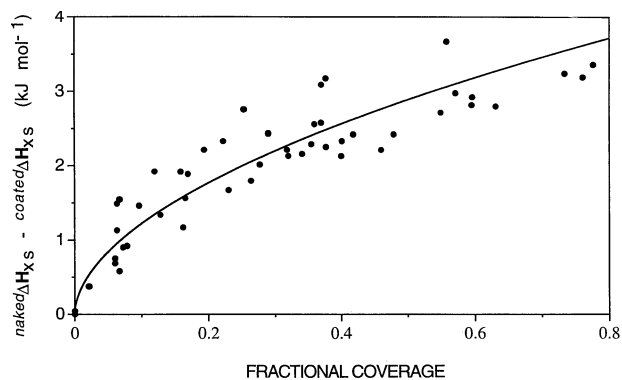


Fig. 5. The difference in ΔH_{xs} between the organically coated solid and naked (uncoated) endmember and the fractional coverage of the surfaces as calculated from molecular dimensions and molar adsorption. Experimental systems plotted here include all four fatty acids, adipic acid and CPB on alumina, and CPB on silica and oxidized marine sediment. The CPB-alumina data set is not included. Solid line represents the power regression of pooled data.

propriate, flat lying, molecular cross section and concentration of adsorbed organic compounds. The resultant reparameterization (Fig. 5) shows that most experimental data fall into a remarkably similar envelope, showing a consistent change in gas adsorption energetics with progressive coverage of surfaces, independent of organic compound or oxide surface. The data for the CPB alumina system were not used for this calculation. The data for the other systems were pooled and subjected to a power regression (solid line), which has the relationship:

$$\Delta(\Delta H_{xs})_{\text{naked-coated solids}} = 4.19 (\text{Fractional coverage})^{0.535} \quad (3)$$

Reduction in the excess enthalpy of nitrogen adsorption is thus proportional to the square root of the fractional coverage. This relationship is used below to estimate fractional coverage of natural sediments. The relative uncertainty in prediction of fractional coverage varies with fractional coverage, being roughly the horizontal extent of the data at any given value of $\Delta(\Delta H_{xs})$.

Similar relationships for these different adsorbent-adsorbate systems imply considerable generality for the relationship between ΔH_{xs} and organic matter coverage of alumina and silica dominated surfaces, within the bounds of scatter among calibration curves. This relationship also assumes that organic matter in natural aluminosilicate sediments always adsorbs in order of site energy, as found for the model systems. The caveats are important ones, but given the variation among the adsorbates (cationic, anionic) and adsorbents, it is striking that such similar curves are obtained.

3.3. Application To Marine Sediments

To apply Equation 3 to marine sediments, it is necessary to assess energetics of gas adsorption on sediment with and without its natural organic coating. In other words, what are the $\Delta(\Delta H_{xs})_{\text{naked-coated solid}}$ values for natural marine sediments? A necessary piece of information is accurate determination of ΔH_{xs} on naked mineral surfaces of various sediments. Due to

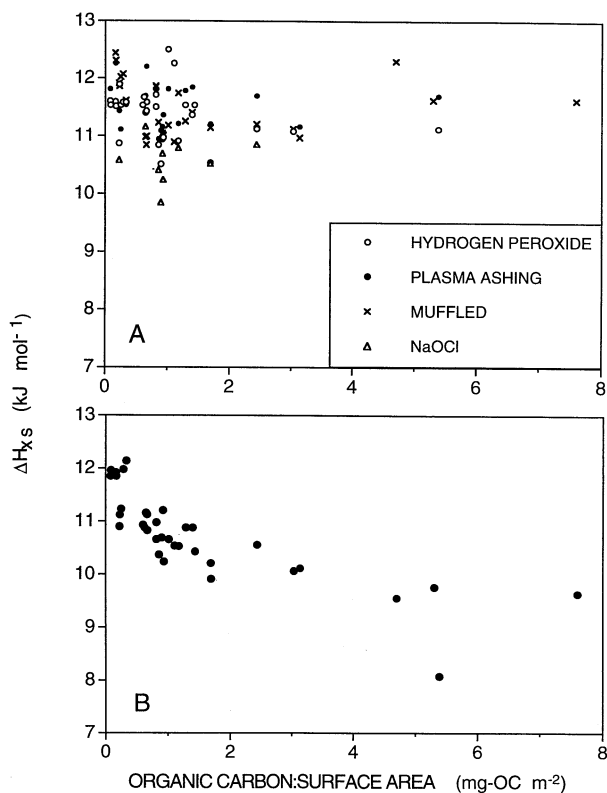


Fig. 6. ΔH_{xs} of N_2 adsorption onto various marine sediments, (a) with and (b) without oxidative removal of their organic matter, versus the organic matter loading in the sediments (as indicated by ratio of organic carbon in the unoxidized sediment to the surface area of the oxidized sediment). The surface area values for the x-axis were those obtained after peroxide attack or muffling, to allow comparison with previously published values.

the considerable variation in C constants of pure oxides representative of those found in sediments (Table 2), it seems desirable to determine naked mineral ΔH_{xs} values for each sediment being examined. This determination requires removal of their natural organic matter coatings in a manner that does not disrupt the surfaces of the minerals.

Four approaches were tried to remove natural organic coatings, all of them oxidative attacks. Two approaches ($H_2O_2/Na_4P_2O_7$ and NaOCl) were liquid phase oxidations, and two (low temperature plasma and 350° oven) were intended to avoid possible artifacts of liquid phase oxidation; e.g., dissolution and corrosion of the mineral surface. The four approaches gave ΔH_{xs} values that were usually within ca. 1 kJ mol^{-1} of one another (Figure 6a). These values are also similar to those of the naked, model oxide surfaces used in the coating experiments (above), which is to be expected because clay minerals that provide the bulk of surface area in marine sediments (Mayer and Rossi, 1982), have alumina and silica surfaces. Lower ΔH_{xs} values were occasionally found for oxidized sediments due to incomplete removal of natural organic matter coatings during the oxidation process. Typically enough organic matter was left after oxidation to yield an organic carbon:surface area ratio (OC:SFA) of $0.08\text{--}0.15 \text{ mg OC m}^{-2}$. Interestingly, these residual organic matter loadings are approximately equal to those observed in deep sea sediments

(Mayer, 1994b), implying a small fraction of organic matter that is very resistant to oxidative attack. Among these four treatments, the NaOCl treatment often gave the lowest ΔH_{xs} values in spite of effective organic matter removal. Possibly the higher pH in this treatment (ca. 9–9.5) caused chemical or microtopographic changes that reduce C constants.

Microporosity (pores smaller than 2nm) can cause high C constants, so their role in influencing variations in ΔH_{xs} among samples was considered. The importance of micropores was assessed using the t-plot method (deBoer et al., 1966). The results indicated that no more than 10% of the total gas adsorption could be due to micropores, based on the intercepts of the t-plots (data not shown). However, two factors suggest that even these values might be artifactually high. First, there was no downward bending of the t-plots at low partial pressures, a characteristic sign for microporosity. Second, correct application of the t-plot method requires knowledge of the appropriate nonporous reference isotherm for the porous solid under consideration (Lecloux and Pirard, 1979). Both positive and negative intercepts were found for the oxidized marine sediments examined here. Because negative intercepts are impossible if the correct reference isotherm is used (Lecloux and Pirard, 1979), it seems likely that variations in the applicable reference isotherm for various sediment surfaces are sufficient to cause a $\pm 10\%$ variation in the microporosity determined from t-plot intercepts. The dilemma therefore arises that a correct reference isotherm for each sediment is impossible to determine, because it depends on the C constant of the material and yet the C constant is possibly affected by microporosity. At the level of potential microporosity observed here ($<10\%$ of the gas adsorption), the result is a circular argument with no resolution. The small variations in ΔH_{xs} among the oxidized sediments in Fig. 6a may, therefore, be due to changes in surface topography (e.g., micropores) or chemical aspects of the surface. However, microporosity does not appear to have significant influence on gas adsorption energetics with these samples.

Sediments with their original organic matter coatings show a strong inverse correlation between ΔH_{xs} values and the OC:SFA ratio (Figure 6b), unlike their oxidized versions (Fig. 6a). The trend in Figure 6b holds whether surface area values from untreated or peroxide treated samples are used to calculate OC:SFA. The peat sample, unoxidized, had a ΔH_{xs} of 7.8 kJ mol^{-1} , but there was insufficient mineral material for surface area determination of its oxidized subsample. These contrasting trends (Fig. 6a vs. 6b) indicate that C constant measurements respond to natural organic matter concentrations, and not to the mineral phases.

The naked mineral ΔH_{xs} values (i.e., from oxidized subsamples) can be used with the ΔH_{xs} values for the unoxidized subsamples of sediment to obtain an estimate of the fractional coverage of the sediment by its natural organic matter, using equation (3). Several sediments with low OC:SFA ratios had slightly higher H_{xs} values (by $<0.5 \text{ kJ mol}^{-1}$) for the unoxidized than the oxidized samples, which would yield a negative surface coverage. These negative surface coverages result from scatter in the oxidized samples, and hence data from these samples are not considered. For the sake of clarity, only the peroxide treated and muffled samples are presented here to provide examples of results obtained by dry and wet oxidation

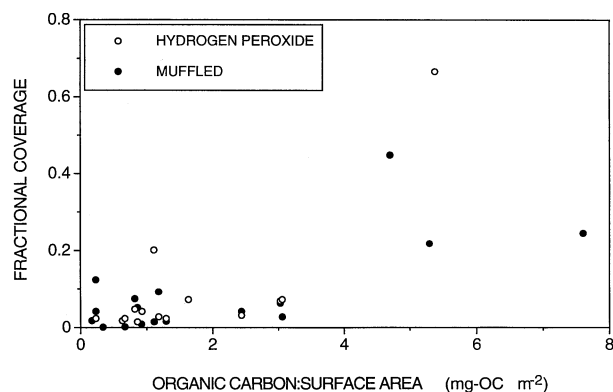


Fig. 7. Fractional coverage of sedimentary mineral surfaces vs. their organic carbon:surface area ratio. Coverage calculated from equation (3), using ΔH_{xs} (naked-coated solid) calculated from samples treated with either hydrogen peroxide (open circles) or muffling (closed circles) to obtain the naked sediment value for ΔH_{xs} .

(Figure 7). Similar results would obtain with the plasma and hypochlorite treated samples.

These calculations (Figure 7) show that all sediments with OC:SFA ratios $< 3 \text{ mg-OC m}^{-2}$ have very small fractional coverages. All of the samples with monolayer equivalent levels of OC (OC:SFA = $0.6\text{--}1.5 \text{ mg-OC m}^{-2}$) have less than 22% of their mineral surfaces covered. Hence, the mineral phases in these sediments are essentially uncovered by natural organic matter. There is less correlation between the extent of coverage at OC:SFA values of $< 3 \text{ mg-OC m}^{-2}$ and the OC:SFA ratio than was found for the ΔH_{xs} of the unoxidized sediment (Fig. 6b). This loss of progressive change is likely due to noise induced by factoring the oxidized, and hence uncoated, sediment values into the calculation. Using a single naked sediment value of ΔH_{xs} for all samples would have preserved a more significant relationship. No significant correlations were found among the fractional coverages calculated from the four different oxidation treatments, suggesting that random error dominates these values. However, the low values found for all approaches provide confidence that the primary conclusion of low surface coverage is accurate. These low coverages are consistent with the generally small influence of organic matter removal on sediment surface area measurements (Mayer, 1994a).

Sediments with higher OC:SFA ratios have greater fractions of their surfaces dominated by organic matter (Figure 7), according to this calculation. The peat sample from Alaska was not plotted because its oxidized sediment could not be measured due to lack of material. Its ΔH_{xs} value was 7.8 kJ mol^{-1} , similar to that of the Skan Bay (2–4 cm) sediment, and consistent with dominantly organic surfaces. The results from these high OC:SFA samples build confidence that more extensive organic coatings on low OC:SFA sediments could have been detected by this method. Marine sediments with OC:SFA ratios of $> 3 \text{ mg-OC m}^{-2}$ are quite rare in the ocean (Mayer, 1995) so that the finding of largely naked mineral surfaces applies to virtually all marine sediment.

3.4. Geochemical Implications

Although organic matter is clearly associated with mineral grains (Mayer et al., 1993; Mayer, 1994a; Keil et al., 1994), it

is also clearly not adsorbed in a monolayer. Patches of organic matter must be localized on mineral surfaces, and must be thicker than a monolayer would imply. Monolayer adsorption has been recognized as a possible configuration for several decades (Weiler and Mills, 1965; Suess, 1973; Tanoue and Handa, 1979; Mayer 1994a,b; Keil et al., 1994). Ransom et al. (1997) recently challenged this interpretation on the basis of transmission electron microscopic examination of sedimentary mineral grains. While it is not clear that monolayers would have been visible using their approach even if present, the data presented here support their conclusion. The term monolayer equivalent should therefore be removed from usage, lest it imply a situation that is clearly not the case.

The localization of these patches of organic matter associated with minerals is an important area for future study. Kubicki et al. (1997) suggested that adsorption of organic matter occurs primarily at edge sites of clay minerals. Given aspect ratios of clay platelets ranging from 10–100, the fractional coverage data presented here are consistent with this model. The mesopore protection hypothesis (Mayer 1994a,b), wherein organic matter is protected by its incorporation inside mesopores too small to allow enzymatic attack, is dependent on this localization. Most surface area appears to be within mesopores of $< 10 \text{ nm}$ diameter, as evidenced by pore size analysis (Mayer 1994a), and hence the possibility remains that most sedimentary organic matter lies within these smaller pores. The localization may be associated with distinct compositional phases, such as highly sorptive iron oxyhydroxide phases.

The configuration of organic matter has important implications for the adsorption and desorption rates of contaminants. Lack of dispersal over all mineral surfaces suggests thicker blebs of organic matter, and provides some constraints on diffusion models (e.g., Wu and Gschwend, 1986; Hunter et al., 1996).

The reactivity of minerals with aqueous solutions can be significantly inhibited by organic coatings (e.g., Welch and Vandevivere, 1994; Thomas et al., 1993). The partial organic coverages inferred here might therefore be interpreted as allowing most of the mineral surface to be exposed to exchange with solution. However, it is quite possible that interfacial reactions are significantly inhibited by the 1%–10% coverage found here, if the sites covered are the reactive ones. The relatively sharp dropoff in gas adsorption energy with initial coatings of organic matter in our model system experiments are consistent with preferential fouling of sites reactive to physisorption. If these higher energy sites are similarly important for gas adsorption and the geochemical reactions under consideration, then poisoning of surface reactivity, rather than full armoring of surfaces, will result from these organic matter–mineral interactions.

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