

THE ADSORPTION PROTECTION THEORY: AN EXAMINATION OF
TWO MARINE ENVIRONMENTS; THE CONTINENTAL SLOPE ALONG
SOUTHWESTERN VANCOUVER ISLAND, BRITISH COLUMBIA AND THE
CONTINENTAL SHELF AND SLOPE OF THE MAKRAN AREA ALONG THE
COAST OF PAKISTAN.

by

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We accept this thesis as conforming
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Abstract

The model of adsorption of organic matter onto sediment surfaces is increasingly being used to explain enhanced preservation of organic matter in marine sediments. While recent studies have shown that there is strong evidence that sediment surfaces play a role in protecting organic matter from microbial degradation, these same studies have looked primarily at marine environments that could be considered "ideal," whereby there exists plenty of organic matter production, consistent sedimentary inorganic material input and no post-depositional disturbance of the sediment and organic material.

The continental slope along the southwestern coast of Vancouver Island, British Columbia, and the continental shelf and slope of Makran area of the Arabian Sea, along the coast of Pakistan, are regions in which there is moderate to high primary productivity and varying sediment input and redistribution regimes. The continental slope of the southwestern coast of Vancouver Island can be characterized as sediment starved region, the majority of riverine sediments are captured in the coastal fjord system and there is very little aeolian input. The sediments that are deposited along the coast of Vancouver Island have been classified as relict deposits and undergo re-suspension and re-distribution events as a result of both tectonism and interactions with bottom water currents. The continental shelf and slope of the Makran area of the Arabian Sea varies from the continental slope of Vancouver Island in that there is plenty of sediments supplied via rivers along the coast of Pakistan, India, and Iran. Furthermore, the Makran area is subject to inputs of aeolian deposits from the surrounding deserts. Similar to the

coast of Vancouver Island, the Makran area is subject to tectonism and bottom water and storm currents re-suspending and re-distributing sediment.

Organic matter production along the coast of Vancouver Island ranges from 150 – 200 g C m⁻² year⁻¹, while organic matter production in the Makran area of the Arabian Sea ranges from 200-400 g C m⁻² year⁻¹. The percentage of organic matter preserved on the continental slope of the southwestern coast of Vancouver Island and the continental shelf and slope of the Makran area ranges from 0.36 – 0.77% and 0.50 – 2.48%, respectively.

Bulk sediment surface area for samples from the continental slope of the southwestern coast of Vancouver Island and the continental shelf and slope of the Makran area range from 11.6 – 24.6 m²/g and 10.0 – 24.8 m²/g, respectively. There is no correlation between surface area and organic carbon concentrations for either region. Samples from the continental slope of the southwestern coast of Vancouver Island have surface area to organic carbon concentration ratios that fail to meet the limits set for monolayer equivalence. Samples from the continental shelf and slope of the Makran area of the Arabian Sea, on the other hand, have surface area to organic carbon concentration ratios that fall within the limits set for monolayer coverage of the individual sediment grains by organic matter, however when their fractional coverage was calculated the majority of samples were <22% coated by organic matter.

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Dedication

I wish to dedicate this thesis to the memory of my grandfather,
George R. Patterson (PaPa), 1921-2001.

The greatest gift he ever gave me was knowledge and
without him I would have not had this undying thirst for knowledge,
for that I am eternally grateful.

and

I wish to also dedicate this thesis to my canine comrade, Lucky, she was always
ready for a stress relieving hike at the drop of a hat.

and

I wish to dedicate this thesis to my mum.

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Chapter 1 - Introductory Statement

Introduction

The fate of sedimentary organic matter in the marine environment has been of great discussion in paleo-environmental and petroleum source rock studies over the past several decades. Sedimentary marine organic matter is an important source for fossil fuels (Parrish, 1982) and is useful as an environmental indicator (Keil et al., 1994). It has long been known that marine derived organic matter is the primary source for oil (Parrish, 1982). Considering that approximately 1% of the total organic matter produced and or supplied to the surface ocean is preserved in marine sediment, the mechanisms by which organic matter preservation occur become increasingly important (Demaison and Moore, 1980; Suess, 1980; Hedges and Keil, 1995, Hedges et al., 1997), especially when trying to understand the distribution of petroleum source rocks (Ibach, 1982; Parrish, 1982; Adams and Bustin, 2001).

An incomplete understanding of the factors that control the preservation and content of organic matter in marine sediments has created complications for a number of studies (Keil et al., 1994). Table 1 provides a brief overview of some of the controlling factors on marine organic matter preservation. The predominant view, with respect to organic matter preservation, during the late 1970s and 1980s, was that organic matter accumulation was primarily the result of anoxic bottom waters decreasing the rate of decay of organic matter via slowing the metabolism of microbes and therefore leading to enhanced preservation of organic matter. While there is enhanced organic matter

preservation in regions with sub-oxic to anoxic bottom water (Demaison and Moore, 1980), this theory does not fully account for organic matter accumulation observed in oxygen rich regions, such as along continental shelves, outside the oxygen minimum zone (Calvert et al., 1992; Pedersen et al., 1992; Calvert and Pedersen, 1993; Calvert et al., 1995; Ganeshram et al., 1999). Furthermore, the notion that anoxia either ceases or inhibits organic matter decomposition is not entirely valid, since some anoxic basins have decomposition rates of organic matter that have been determined to be comparable to decomposition rates under oxic conditions (Demaison and Moore, 1980; Canfield, 1989). Therefore, regardless of the redox conditions of the sediment and or the water column, other mechanisms must be acting to increase the preservation potential of organic matter.

Sedimentation rate has been discussed as a primary control on organic matter preservation, especially in oxic environments (Muller and Suess, 1979; Demaison and Moore, 1980; Canfield, 1989; Calvert et al., 1992; Calvert and Pedersen, 1992; Pedersen et al., 1992). In oxic regions such as the Argentine basin, the northwest African continental margin, and the deep regions of both the North Pacific and North Atlantic Oceans there is a positive correlation between sedimentation rate and organic carbon concentration (Demaison and Moore, 1980). The sedimentation rate is considered critical as it controls the rate of time that an organic particle spends in the zone of intense microbial degradation. In regions of high sedimentation rates a greater amount of organic matter is preserved in the sediment (Muller and Suess, 1979; Ibach, 1982). Ibach (1982) found that organic matter deposited under fairly rapid sedimentation rates showed very few signs of aerobic or anaerobic degradation, while organic matter deposited under very low sedimentation rates was likely to be completely destroyed. Furthermore, Ibach

(1982) has determined that organic matter preservation increases with increasing sedimentation rates up to a critical rate at which point the amount of organic matter preserved decreases with increases in sedimentation rate, which is likely the effect of dilution of organic matter by clastic sediment. However, much like the anoxia theory, sedimentation rates do not fully account for the vast amounts of organic matter that is being preserved in many marine sediments.

Since the introduction of the theories of preservation via anoxic bottom waters reducing microbial metabolism and preservation via sedimentation rate, there have been a number of mechanism or controlling factors that have been proposed to enhance organic matter preservation: 1) the rate at which organic matter production occurs in the overlying water column (Calvert et al., 1992; Calvert and Pedersen, 1992; Pedersen et al., 1992; Calvert and Pedersen, 1993; Calvert et al., 1995; Bergamaschi et al., 1997); 2) the sources of inorganic and organic material (Weiler and Mills, 1965; Demaison and Moore, 1980; Hedges et al., 1997); and 3) the effect surface area of inorganic particles might have in sequestering organic matter from microbial decay (Weiler and Mills, 1965; Keil et al., 1994b; Mayer, 1994a; Mayer, 1994b; Hedges and Keil, 1995a; Hedges and Keil, 1995b; Ransom et al., 1997; Ransom et al., 1998; Cowie et al., 1999; Mayer, 1999; Arnarson and Keil, 2000; Baldock and Skjemstad, 2000; Bock and Mayer, 2000; Adams and Bustin, 2001; Arnarson and Keil, 2001).

Rate of organic matter production

Calvert et al. (1995) suggest that while sedimentation rate is the primary mechanism controlling organic matter preservation, the rate of organic matter production should be considered a secondary mechanism. Preservation of organic matter in this case

occurs as a result of high organic matter production within the photic zone, thus creating a greater than average export of organic matter to the sea floor, thereby increasing the concentration of organic carbon in the underlying sediments. Consequently, in an upwelling nutrient rich region, such as along the coast of Peru, higher rates than average result in considerable quantities of organic matter being exported to the sediment. On the other hand, in a nutrient poor region, such as in the middle of the Sargasso Sea or the middle of the Southern Pacific, there is lower than average productivity resulting in very low preservation of organic matter in the underlying sediment. However, Keil and Cowie (1999) found in the northeastern region of the Arabian Sea, where there is considerable primary production, there is little correlation between high productivity and increases in organic carbon preservation in the underlying sediment.

Organic matter sources

Terrestrial and marine organic matter can share similar properties, however for the most part they are very different. Marine organic matter is composed of simple organic compounds which can be readily and efficiently degraded within the top 500 m of the ocean (Hedges and Keil, 1995a), whereas terrestrial organic matter contains lignin, hemicellulose, taninnins, resins, cuticular waxes, cutin and suberin, which can be very persistent and tough to degrade (Hedges et al., 1997). Terrestrial organic matter is delivered to the ocean, typically, by way of rivers and upon reaching the ocean the terrestrial organic matter consists of highly degraded, nitrogen poor, remains of plants (Hedges et al., 1997). The highly degraded organic matter would, therefore, likely be preserved, as the portion delivered to the ocean would be refractory and almost equivalent to kerogen, depending on how long the transport of the terrestrial organic

matter had taken (Hedges et al., 1997). Though, terrestrial organic matter does not appear to be a large constituent of marine sediments, with the exception of deltas and some fjord systems. Particulate terrestrial organic matter appears to be persistent and more resistant to degradation over time, while dissolved terrestrial organic matter does not appear to be as easily preserved (Hedges et al., 1997). Therefore the type of organic matter, whether it be marine derived organic matter or terrestrial organic matter or in particulate or dissolved form appears to be important with respect to enhancing the preservation potential of organic matter.

Organic matter – surface area relationship

Weiler and Mills (1965), Demaison and Moore (1980), Suess (1980), Parrish (1982), Ibach (1982), and Calvert and Pedersen (1992) noted a relationship between organic carbon concentrations and fine grained sediment, which could be considered a proxy for the surface area and organic carbon relationship which has been the focus of many recent studies (Mayer et al., 1988; Keil et al., 1994b; Mayer, 1994a; Mayer, 1994b; Bergamaschi et al., 1997; Adams and Bustin, 2001). Up until the past five years the surface area-organic carbon correlation has been ascribed to monolayer adsorption of organic compounds onto mineral surfaces (Mayer, 1999; Mayer et al., 2002). The organic matter is proposed to bend, flex and condense across the mineral surfaces thereby covering the sediment grains in a monolayer of organic matter. Though, recently there has been a shift away from this theory of monolayer coverage of individual sediment grain towards a theory proposed by Ransom et al. (1997), which suggested that organic matter is dispersed across mineral surfaces in discrete patches. Regardless of whether the organic matter is adsorbed in discrete patches or as monolayer coating, the adsorption

protection theory relies on the organic matter concentrating itself in pores across the surface of the minerals. These pores have diameter on the order of 2 to 8 nanometres wide (Mayer 1999). The importance of concentrating organic matter into these nano-sized pores is that the organic matter becomes isolated from destructive enzymes which can initiate organic matter degradation, as well the organic matter is isolated from very small microbes which can further assist in their degradation.

This thesis investigates the adsorption protection theory on two continental shelf and slope systems, the Makran region of the Arabian Sea and the southwest coast of Vancouver Island. The two regions chosen have very different oceanographic settings and therefore the role of organic matter adsorption onto mineral surfaces can be evaluated for two different regions that undergo different conditions.

Adsorption

The surface area – organic matter relationship is dependant on the interaction of sedimentary mineral surfaces with organic matter in its dissolved state, and thus the chains of organic matter condense on the surfaces of these mineral grains. Surface area adsorption has been used to explain the occurrence of gas uptake into solids (Gregg and Sing, 1982; Rupert, 2003). Adsorption is defined by Gregg and Sing (1982) and Clarkson (1994) as the enrichment or depletion of one or more components in an interfacial layer. In this case organic matter is being “enriched” onto the surfaces of the sedimentary minerals during the early stage of deposition in the marine environment, therefore the minerals are acting as the adsorbent and the organic matter is the adsorbate.

Adsorption of an adsorbate, such as organic matter, can occur either through physical or chemical adsorption (Gregg and Sing, 1982). Physical adsorption refers to the organic matter adsorbing onto the surfaces of the minerals via dispersive forces, while the chemical adsorption refers to the organic matter adsorbing onto the surfaces of the minerals via electrostatic attraction (Clarkson, 1994). Physical and chemical adsorption have been known to occur both separately, as well as in combination with each other (Gregg and Sing, 1982; Clarkson, 1994; Adams 2003), therefore the interaction between a mineral surface and organic matter can be through either physical or chemical adsorption or via both forces depending on the nature of the adsorbents and adsorbates (Clarkson, 1994).

Understanding the nature of the relationship between organic matter and mineral surfaces is important when determining the fate of organic matter through diagenesis. If the forces causing adsorption are physical in nature, then the adsorption of organic matter onto the mineral surfaces is likely to be easily reversed. Whereas if adsorption occurs chemically, then the adsorption of organic matter onto the mineral surfaces creates a much stronger bond and requires much more energy for desorption to occur, then if the adsorption of organic matter were physical in nature. Whether the organic matter is adsorbed chemically or physically becomes very important when considering the fate of the organic material during diagenesis. Physically adsorbed organic matter is likely to be easily desorbed, thereby allowing the organic matter to become susceptible to microbial attack.

Organic Matter Preservation, Surface Area Interaction

The relationship between organic matter and surface area has been shown in studies by Bishop et al. (1992), Keil et al. (1994b), Mayer (1994a), Mayer (1994b), Hedges and Keil (1995a), Ransom et al. (1997), Keil and Cowie (1999), Kaiser and Guggenberger (2000), Adams and Bustin (2001), and Arnarson and Keil (2001) to be quite a compelling means for enhancing organic matter preservation. The prevailing idea is that as sediment surface area increases, so to does the concentration of organic matter of a given sediment sample (Mayer, 1994a; Mayer, 1994b), thus the organic matter appears to be associated with high surface area type minerals such as clays.

Within the water column, prior to reaching the sediment and within the top few centimeters of the sediment, terrestrial and or marine organic matter becomes adsorbed onto mineral surfaces during deposition. The organic matter has been proposed to be associated with intragranular micropores (<2 nm) and mesopores (2-50 nm), thereby isolating the organic matter from hydrolytic enzyme degradation and further microbial degradation as both hydrolytic enzymes and microbes tend to be too large to effectively fit into micropores and some mesopores (Mayer, 1994b).

While there is ample evidence from recent studies that surface area acts to enhance organic matter preservation, the manner in which organic matter is adsorbed to the sediment surfaces is of considerable debate. There are two schools of thought, with respect to the organic matter – sediment surface interaction. Organic matter is believed to either coat the entire surface of each individual mineral grain (Keil et al., 1994a; Mayer,

1994a; Mayer, 1994b; Hedges and Keil, 1995a) or be adsorbed in discrete patches over the mineral surface (Ransom et al., 1997; Mayer, 1999).

Mayer (1994b) proposed that the interaction between organic matter and mineral surfaces behaved in such a way that the organic matter would coat the surfaces of the mineral grains with a monolayer coating. Complete coverage of a mineral grain had, therefore, been named the monolayer equivalence level, or the concentration of organic carbon per square metre that covers the entire mineral surfaces (Mayer, 1994a; Mayer, 1994b). Mayer (1994b) saw the monolayer equivalence level as a maximum coating potential for a mineral grain, having a range from 0.5 to 1.0 mg OC m⁻².

Since Mayer's (1994a; 1994b) proposal of a monolayer coating of organic matter, Ransom et al. (1997) observed in transmission electron microscopy that organic matter did not actually exist as a single coating across a mineral grains surface, rather they found that the organic matter was adsorbed in discrete patches across a mineral surface and that the organic matter was associated with topographic lows on the mineral surfaces. Furthermore, Mayer (1999) examined the extent of organic matter coverage across the mineral surface via examining the fractional coverage of the mineral grains. Mayer (1999), Mayer and Xing (2001) and Mayer et al. (2002) determined that for the samples they analyzed the fractional coverage is only 22%, even though the same samples fell within the monolayer equivalence range established by Mayer (1994a; 1994b). Mayer (1999) has concluded that the monolayer equivalence level, established by Mayer (1994a; 1994b), has no bearing on whether organic matter is coating individual mineral grains as single layer or as discrete patches. Organic matter is more likely to be associated with

high enthalpy adsorption sites, thus organic matter tends to adsorb onto mineral surfaces in patches as the surface of a mineral grain tends to have enthalpy variations (Mayer, 1999).

Thesis Structure

The following thesis focuses on the relationship between organic matter and surface area and the relevance of this relationship with respect to enhancing organic matter preservation. The following chapters focus on two very different oceanographic settings in order to determine how applicable the organic matter – surface area relationship is when environmental variables are changed.

Chapter 2 focuses on a region along the southwest coast of Vancouver Island, where there is moderate organic matter production driven by seasonal upwelling events, low terrestrial input of inorganic sediment, and sediment redistribution post settling.

Chapter 3 focuses on the continental shelf and slope of Makran area, along the coast of Pakistan in the Arabian Sea. The Makran area is characterized by high organic matter production driven by monsoonal events and high inorganic material input. Chapter 3, also, explores the conundrum of whether organic matter is adsorbed as a distinct monolayer, as observed by Mayer (1994a; 1994b), or if the organic matter preferentially adsorbs to high enthalpy sites on mineral surfaces, as observed by Ransom et al. (1997), Mayer (1999), Mayer and Xing (2001) and Mayer (2002), thus adsorbing in discrete patches.

Chapter 4 is a summary chapter that combines offers a brief summary for both chapters 2 and 3, as well as a brief comparison of the two study regions with respect to organic matter preservation enhancement via adsorption protection.

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Table 1: Table of mechanisms and controlling factors on organic matter preservation in the marine environment.

Conditions That Affect Organic Matter Preservation	Description	Source
Anoxia	Anoxic marine environments have dissolved oxygen concentrations of less than 0.5 ml / L. In anoxic regions aerobic microbes cannot rapidly degrade the organic matter and benthic scavenging cannot occur as there is not enough oxygen. Anaerobic microbial decay of organic matter is typically much slower than aerobic microbial decay, therefore organic matter is preserved quite effectively	Demaison and Moore 1980
Sedimentation Rate Low Sedimentation Rate Moderate Sedimentation Rate High Sedimentation Rate	Organic matter at the sediment-water interface is left exposed to microbial decay, given the right conditions. Therefore in an environment where sedimentation rates are low, the amount of organic matter preserved is low. Organic matter is getting buried shortly after it has settled and is isolated from being readily consumed by microbes and benthic scavengers, organic matter preservation is much better than in low sedimentation rate environments. Organic matter is diluted by the sediment, the organic matter is isolated from microbial decay and scavenging.	Demaison and Moore 1980; Ibach 1982; Parrish 1982

Table1: Table of mechanisms and controlling factors on organic matter preservation in the marine environment.

Conditions That Affect Organic Matter Preservation	Description	Source
<p>Organic Matter Supply</p> <p>No overlying organic matter production</p> <p>Moderate organic matter production</p> <p>High organic matter production</p>	<p>No primary production means that there is no export of organic matter from the surface mixed layer to the underlying sediments, therefore no organic matter preservation.</p> <p>Moderate production in the surface mixed layer means that a moderate amount of organic matter is exported to the underlying sediments, therefore a moderate amount of organic matter is preserved. NOTE: during sedimentation of the organic matter, the organic matter is exposed to microbial decay as well as consumption by zooplankton, fish and other organisms</p> <p>High production in the surface mixed layer means that a large quantity of organic matter is exported to the underlying sediments, therefore a large amount of organic matter is preserved. NOTE: during sedimentation of the organic matter, the organic matter is exposed to microbial decay as well as consumption by zooplankton, fish and other organisms.</p>	<p>Calvert et al., 1992; Calvert and Pedersen, 1992;</p> <p>Pedersen et al., 1992; Calvert et al., 1995</p>
<p>Organic Matter Source</p> <p>Marine</p>	<p>Marine organic matter is mainly lipid rich material. The primary source of marine organic matter is primary producers, or phytoplankton. Marine organic matter is typically more labile than terrigenous organic matter and is composed of simple organic chains.</p>	<p>Hedges et al., 1997;</p>

Table1: Table of mechanisms and controlling factors on organic matter preservation in the marine environment.

Conditions That Affect Organic Matter Preservation	Description	Source
Organic Matter Source Terrigenous	Terrigenous organic matter is made up of waxes, cutins, and other complex organic compounds. Terrigenous organic matter is distributed by way of rivers. Depending on transport time, the organic matter is degraded to varying extents with labile organic material being removed preferentially leaving the more refractory portion to be distributed to the continental shelf and slope. Because of the refractory nature of terrigenous organic matter and the type of organic matter, terrigenous organic matter is less likely to be degraded.	Continued...
Pelittization via marine organisms	Marine organisms such as fish and zooplankton take up organic matter in the form of phytoplankton or other zooplankton. The organic material is partially used by the organism to create energy while the rest of the organic matter is formed into fecal pellets which are excreted by the organism and settle to the sea floor at an increased rate. Some of the organic matter is recycled while a small portion is preserved via pelittization in the sediment.	Adams and Bustin, 2001
Adsorbption onto mineral surfaces	Organic matter is adsorbed onto mineral surface through physical and or chemical sorption. The adsorbed organic matter is sequestered in micro- and meso- pores. The pores on the mineral surfaces act to "block" any enzymic reactions and microbial decay, as most enzymes and microbes are greater in size than the pores on the mineral surface. With the organic matter adsorbed onto the surface the organic matter and mineral particle is denser than the two components seperated therefore the mineral particle and organic matter would sink faster after adsorption. Rapid removal of organic matter from the water column and "sequestration" from enzymic and microbial decay.	Weiler and Mills, 1965; Mayer, 1994a; Mayer 1994b; Hedges and Keil, 1995ab; Ransom et al, 1997; Adams and Bustin, 2001

Chapter 2 - Sediment surface area control on organic matter preservation on the continental slope of southwestern Vancouver Island

Abstract

The relationship between bulk sediment surface area and organic carbon concentration are examined for sediments from the eastern Pacific Ocean on the continental slope along the southwestern coast of Vancouver Island. Recent studies have found strong correlations between sediment surface area and organic carbon concentrations in both marine sediments and soils, giving rise to the conclusion that sediment surfaces act to protect organic matter from degradation via microbes during deposition and the subsequent stages of diagenesis. The continental slope of the southwestern coast of Vancouver Island is an ideal local to test the relationship between sediment surface area and organic carbon concentrations as this region receives a moderate amount of organic carbon input via primary production, however the continental shelf and slope are considered sediment starved.

The overlying water experiences primary production rates on the order of 150 – 200 g C m⁻² year⁻¹, of which only a fraction is preserved in recent sediments: organic carbon concentration on the continental slope range from 0.36 – 0.77%. The inorganic sediment input into this region is hampered by the extensive coastal fjord system, which acts to trap terrigenous sediment input to the open ocean. Comparisons between bulk sediment surface area and organic carbon concentrations have shown that no correlation can be made between these two variables, and therefore organic carbon preservation is not being enhanced nor assisted by adsorption onto sediment surfaces.

Introduction

Of the total organic matter supplied to the surface ocean, only approximately 1% is preserved in marine sediments, whilst the other 99% is remineralized and recycled efficiently, within the water column and within the surface sediments, as nutrients for bacteria and other organisms (Suess, 1980; Hedges and Keil, 1995a; Hedges et al., 1997; Adams and Bustin, 2001). Sedimentary organic matter is important for the determination of the provenance, depositional history, and resource potential of marine sediments, therefore understanding the preservation of organic matter is essential. The preservation of organic matter in marine sediments has been the focus of many studies over the past several decades and yet there is no definitive answer as to which mechanism or mechanisms are responsible for enhanced preservation.

In the late 1970s and early 1980s, the predominant theory related to organic matter preservation was that the anoxia in the overlying water column and sediment column was the key controlling factor (Demaison and Moore, 1980). Studies of many basins have shown that there is a relationship between low bottom water oxygen concentrations and enhanced organic matter preservations, however in some basins decomposition of organic matter under anoxic conditions has been shown to occur at rates comparable to those under oxic conditions (Canfield, 1989).

While sedimentation rates are thought to be a primary controlling factor on organic matter preservation, there are several studies debating the secondary controls on organic matter preservation. Therefore in order to explain how organic matter

preservation is enhanced other mechanisms, such as: 1) inorganic and organic sediment sources (Weiler and Mills, 1965; Demaison and Moore, 1980; Hedges et al., 1997); 2) the rate of organic matter production in the overlying water column (Calvert et al., 1992; Pedersen et al., 1992; Calvert and Pedersen, 1993; Calvert et al., 1995; Bergamaschi et al., 1997); 3) sedimentation rates (Demaison and Moore, 1980; Calvert et al., 1992); and 4) sediment surface area (Weiler and Mills, 1965; Keil et al., 1994b; Mayer, 1994a; Mayer, 1994b; Hedges and Keil, 1995a; Cowie et al., 1999), have been proposed.

In the past decade the relationship between sediment surface area and organic matter has been considered to play a major role on organic matter preservation, and the adsorption protection theory has been employed.

The adsorption protection theory

Organic matter from both terrigenous and marine source comes into contact with the inorganic sediment particle surfaces. The organic matter is adsorbed onto the sediment surface, once adsorbed, organic matter is believed to be sequestered from biological remineralization. The adsorbed organic matter and sediment settle through the water column at a higher rate than the organic matter would on its own, increasing the chance that the organic matter will be protected from degradation during settling. The adsorption protection theory is based on the observation that in marine sediments and some soils as surface area increases so to does the concentration of organic matter (Mayer, 1994a; Mayer, 1994b). Strong correlations between organic matter and surface area has been shown by Bishop et al. (1992), Keil et al. (1994b), Mayer (1994a), Mayer

(1994b), Hedges and Keil (1995a), Ransom et al (1997), Keil and Cowie (1999), Kaiser and Guggenberger (2000), Adams and Bustin (2001), and Arnarson and Keil (2001).

The organic matter is believed to adsorb as either a discrete single layer coating the entire mineral surface, a monolayer coating (Weiler and Mills, 1965; Mayer, 1994b) or as patches across the mineral surface (Bishop et al., 1992; Ransom et al., 1997; Mayer, 1999; Mayer and Xing, 2001; Mayer et al., 2002). The complete coating of a mineral grain is the monolayer equivalence level, or the concentration of organic carbon per square metre of the mineral surface, which is considered the maximum coating potential of a mineral grain (Mayer, 1994a; Mayer, 1994b). The monolayer equivalence level ranges from 0.5–1.0 mg OC m⁻² (Mayer, 1994a; Mayer, 1994b). If the organic matter is, instead, adsorbed in patches, then the organic matter is believed to be adsorbed into intragranular mesopores (2 to 50 nm) and micropores (< 2 nm) (Mayer, 1994a; Mayer, 1994b; Ransom et al., 1997; Bock and Mayer, 2000), or onto high enthalpy adsorption sites (Mayer, 1999).

The continental margin along the southwestern coast of Vancouver Island provides an opportunity to study organic matter preservation in a region of moderate to high primary productivity and low inorganic sediment input. This study examines continental margin sediments to determine if the adsorption protection theory is valid in explaining enhanced organic matter preservation.

Background

Vancouver Island

Western Vancouver Island consists of the northwest-southeast trending Insular Mountains with peaks up to 2200 meters that are composed of deformed Paleozoic and Mesozoic volcanic, plutonic and sedimentary rocks overlain by Tertiary clastic sediments. The Insular Mountains are heavily glaciated and are the main sources of terrigenous sediments deposited in the deep sea west of British Columbia (Herzer and Bornhold, 1982; Blaise et al., 1990). Glaciation has also carved out numerous fjords along the Vancouver Island coastline that trap most terrigenous sediment.

The continental shelf west of the Vancouver Island coastline is relatively narrow (Figure 1), ranging from 5-60 km from the coast to the shelf edge. The inner continental shelf in this region is nearly horizontal, gently sloping seaward ($0-0.2^\circ$), with the exception of abrupt changes in topography such as troughs and canyons that cut into the continental shelf. The outer continental shelf has a slope of greater than 0.2° , whilst the continental slope is much steeper having a slope of $7-15^\circ$. The shelf edge varies in water depth from 190 to 225 meters.

The distribution of sediments and nutrients along the west coast of Vancouver Island are affected by non-tidal currents, tidal current and wave action. The principle, non-tidal, current systems influencing the region off southwestern Vancouver Island is the eastward flowing sub-Arctic gyre, which splits into the southward flowing California current and the northward flowing Alaskan current near the continental margin. The divergence of these two currents occurs between 46°N and 50°N depending on the season (Figure 2). Mean winter surface velocities related to these currents range from 10 to 30

cm/s to the north and 20 cm/s to the south, current velocities tend to decrease in the summer to nearly half the mean winter velocity. The southward flow of the California current along the Vancouver Island coast generates a coastal upwelling zone that brings oxygen poor-nutrient enhanced intermediate water toward the ocean surface. The coastal upwelling, thus, increases primary productivity by increasing the availability of nutrients to organisms within the surface waters. The non-tidal currents, such as the California current, have little effect on sediment transport and redistribution.

The principle tidal current system influencing the west coast of Vancouver Island has a north to northwest current direction with near bottom current velocities of up to 50 cm/s year round. Along with tidal current and gyre currents, wave energy is also important and dominates the western coastline of Vancouver Island. The waves in this region have long periods, up to 20s, and have been known to exceed 15 metres in height; the average wave height in the winter is 4 metres. Tidal current and wave energy are primarily responsible for sediment transport and redistribution of sediment along the continental shelf and slope, although both tidal currents and wave energy can also circulate nutrients towards the sea surface.

Surficial sediment distribution along the west coast of Vancouver Island trend from gravel and boulder sized clasts inshore to sands on the mid-shelf to muddy sands on the outer shelf, seaward of the shelf edge, the surface sediments increase in their mud content and decrease in sand content. The sediment found on the continental shelf is primarily composed of terrigenous sediment containing rock fragments of granodiorite, diorite, intermediate basic volcanics, argillite, sandstone, breccia, and chert, as well as mineral fragments such as: plagioclase feldspar, potassium feldspar, quartz, clay minerals

and other minerals. The surficial sediment also contains an appreciable concentration of carbonate shells, derived from marine organisms, along the southwestern coast the carbonate sediment is dominated by planktonic and benthic foraminifera. The concentration of the carbonate sediment is greater near shore and diminishes seaward. Near shore carbonate deposit include bivalve shells and shell fragments.

Sediment distribution across the continental shelf and slope along the coast of Vancouver Island varies from the inner shelf to the continental slope. The sediment along the outer shelf is olive to olive grey muddy sand containing between 10% and 40% mud. Occasionally deposits of gravel are found within the muddy sand deposits, redeposited as a result of the strong tidal currents and storm waves. The sediment found along the shelf edge is clean, fine, well-sorted sands lying seaward of the muddy sand deposits of the outer shelf. The lack of mud along the upper shelf is due to breaking of internal waves over the shelf edge, which removes finer grained clay material and redistributes the material along the continental shelf and slope. Within 10 cm of the sediment water interface the texture and grain size of the sediment changes. There is a glaciomarine sedimentary deposit that is a stiff light grey sandy mud layer with deposits of gravel interspersed through out underlying the surface sediment. The glaciomarine sediments are part of the Pleistocene glacial events. Both the modern marine sedimentary deposits and the glaciomarine sedimentary deposits are petrographically immature, the deposits can be classified as lithic arenites, sublithic arenites, lithic graywackes, and sublithic graywackes depending on their location on the shelf. The immaturity of the deposits reflects a local source for the sediment.

The shelf sediments are, for the most part, relict deposits as a result of the trapping of most modern sediments, originating from Vancouver Island, in coastal fjords (Bornhold and Barrie, 1991). The Fraser River and the Columbia River have both been presumed to provide some sediment to the shelf along the west coast of Vancouver Island. The mouth of the Fraser River opens into the Strait of Georgia, approximately 100 km from the continental shelf. A residence time of 0.8 years for Fraser River fresh water ensures that most the terrigenous detritus and particle-active contaminants are removed before the fresh water would reach the continental shelf (Macdonald and Pedersen, 1991). In summer a fraction of water containing very fine detritus from the Fraser River may escape into the Strait of Jaun de Fuca at neap tides without much mixing, however bottom currents in the Strait of Jaun de Fuca flow inward towards the Strait of Georgia therefore stopping the transport of sediment from the Fraser River to the continental shelf along the west coast of Vancouver Island (Macdonald and Pedersen, 1991).

The Columbia River is 200 km south of the Vancouver Island continental shelf, along the Oregon-Washington state coastline. In the summer the Columbia River plume has been tracked flowing in a southerly direction, whereas in the winter the northwest coastal currents divert the plume northward (Macdonald and Pedersen, 1991). During the transport of Columbia River freshwater north, the freshwater becomes more saline, mixing with saline Pacific Ocean water. The increased salinity of the Columbia River plume, as it travels northward, results in flocculation of sediment particles. Also, during transport of Columbia River derived sediments, filter-feeding organisms ingest and pelletize the majority of sediment particles (Macdonald and Pedersen, 1991). The Strait

of Juan de Fuca acts as a physical barrier to any further transport of sediment further northward (Macdonald and Pedersen, 1991).

Biological sediment sources include both primary production along the continental shelf, as well as within coastal fjords. Rates of primary production for the western coast of Vancouver Island have been estimated at $150 - 200 \text{ g C m}^{-2} \text{ year}^{-1}$, enhancement of primary production occurs at coastal frontal zones and in upwelling areas (Macdonald and Pedersen, 1991). Upwelling of nutrients is persistent and occurs along the shelf edge and across the continental shelf (Denman et al., 1981). The nutrients that are supplied to the surface via upwelling originate in the California Undercurrent (Macdonald and Pedersen, 1991).

Materials and Methods

Sample Collection

Piston cores were retrieved during the JT96 cruise along the western Canadian continental slope aboard the Canadian Coast Guard vessel the John Tully in 1996. Cores were retrieved from water depth of 620 m and 1170 m, JT96-06 and JT96-07 respectively, in a region along the continental slope southwest of Vancouver Island (Figure 1). The piston cores were stored in a freezer unit until sub-sampled. The sub-samples were freeze-dried.

Total Carbon and Total Nitrogen

The samples were analyzed for total carbon and total nitrogen using flash combustion gas chromatography on a Carlo-Erba NA 1500 CNS elemental analyzer. The

operation of the elemental analyzer, composition of the combustion tube, and information on sample preparation are described by Verardo et al. (1990).

Inorganic Carbon

Determination of inorganic carbon, carbonate carbon, was done using a UIC Coulometrics CO₂-coulometer. The samples were dosed with 10% hydrochloric acid, which reacts with the inorganic carbon to release CO₂. The CO₂ is carried to the coulometer via a stream of scrubbed air where the concentration of CO₂ is quantified and integrated to give the inorganic carbon concentration.

Organic Carbon

The organic carbon concentrations were determined by subtracting the inorganic carbon concentration, determined by coulometry, from the total carbon concentration, determined by gas chromatography.

Surface Area

Surface area analysis was done using a Micromeritics® ASAP 2010 surface area analyzer with N₂ adsorption using a multi-point BET (Brunauer, Emmett, Teller) method (Gregg and Sing, 1982). Each sample was degassed at a constant temperature of 350°C for 3 to 4 hours. The samples were then analyzed for surface area using nitrogen gas as the sorbate at liquid nitrogen temperatures. The standard error of the method ranged from 1% to 3%.

Organic Matter Oxidation

Prior to surface area analysis each sample underwent a process to remove organic matter from the sediment surfaces. Three methods of organic matter oxidation were tested to determine which was the most effective method at removing organic matter from the sediment samples: (1) using 30% hydrogen peroxide; (2) using a mixture of sodium pyrophosphate (0.1 M) and 30% hydrogen peroxide (Sequi and Aringhieri, 1977); and (3) using sodium hypochlorite. The method using a mixture of sodium pyrophosphate and hydrogen peroxide was found to remove organic matter more effectively than the other two methods.

The sodium pyrophosphate and hydrogen peroxide method consists of immersing the sediment samples with 0.1 M sodium pyrophosphate and 30% hydrogen peroxide mixture, as described by Sequi and Aringhieri (1977). The samples were placed in a water bath at temperatures ranging from 70–80°C for a time period of 48–96 hours, or until the evolution of CO₂ ceased, during this time aliquots of hydrogen peroxide were added. The samples were then rinsed three times using distilled water to remove residual salts and freeze dried. Various dried samples were analyzed for organic carbon concentration to determine if complete organic matter removal had occurred.

Results

Organic Carbon and Organic Nitrogen

Organic carbon concentration for the Vancouver Island continental slope ranges from 3.37 to 7.66 mg C/g on a dry weight basis. Cores JT96-06 and JT96-07 have similar

concentrations of organic carbon throughout the cores. Both cores show stratigraphic variability on the order of up to 4 mg C/g (Figure 3).

Concentrations of organic nitrogen range from 0.019% to 0.050% on a dry weight basis, both cores JT96-06 and JT96-07 show stratigraphic variability (Figure 4). Core JT96-07 has lower organic nitrogen concentration than core JT96-06, with the exception of samples from 12 cm core depth.

The organic carbon to organic nitrogen ratios for each core is different; core JT96-06 has organic carbon to organic nitrogen ratios ranging from 9.93 to 13.97, while core JT96-07 has organic carbon to organic nitrogen ratios ranging from 12.54 to 40.95. There is greater stratigraphic variability of organic carbon to organic nitrogen ratios for core JT96-07 than for core JT96-06 (Figure 5).

Surface Area

The bulk sediment surface area for the continental slope along the coast Vancouver Island ranges from 11.6 to 24.6 m²/g, both cores show stratigraphic variability (Figure 6). Core JT96-07 varies, stratigraphically, on the order of 13.0 m²/g, while core JT96-06 varies on the order of 8.0 m²/g. The average bulk sediment surface area is slightly greater for core JT96-06, 18.2 m²/g, than for core JT96-07, 17.4 m²/g.

The correlation between organic carbon and surface area for core JT96-06 (Figure 7) is greater than for core JT96-07 (Figure 8), 0.47 and 0.063 respectively.

Discussion

Organic Matter Distribution, Organic Carbon and Nitrogen

The rate of marine primary production across the continental shelf and slope off the coast of Vancouver Island ranges from 150 to 200 g C_{org} m⁻² yr⁻¹ (De Haas et al., 2002), which is comparable to other productive regions around the world, for example the rate of primary production: in the South China Sea is 130 g C_{org} m⁻² yr⁻¹ (Liu et al., 2002); in the Western Sargasso Sea, along the Bermuda-Atlantic Transect, is 110 to 144 g C_{org} m⁻² yr⁻¹ (Anderson and Pondaven, 2003); in the Irish Sea is 136 to 194 g C_{org} m⁻² yr⁻¹ (Gowen and Bloomfield, 1996; Kelly-Gerreyn et al., 2004); in the Cretan Sea is 80 g C_{org} m⁻² yr⁻¹ (Gogou and Stephanou, 2004a; Gogou and Stephanou, 2004b); across the Labrador shelf ranges from 190 to 385 g C_{org} m⁻² yr⁻¹ (De Haas et al., 2002); and across the continental slope in the Celtic Sea ranges from 120 to 162 g C_{org} m⁻² yr⁻¹ (De Haas et al., 2002).

There is no significant difference between the concentrations of organic carbon at core site JT96-06 versus core site JT96-07, on average core JT96-07 has a higher organic carbon concentration than core JT96-06 with a difference of 0.3 mg/g. The stratigraphic variability (Figure 3) observed in both cores is likely the result of either re-suspension and re-settling of the sediment resulting increased organic matter degradation or differences in the amount of overlying productivity over time.

Transportation of appreciable amounts of terrigenous organic matter to the continental shelf and slope of the west coast of Vancouver Island is not believed to occur, even though a number of samples have organic carbon to organic nitrogen ratios that are greater than those that are typical of marine derived organic matter. The organic carbon

to organic nitrogen ratios increase offshore (Figure 5), core JT96-07 has ratios that reach up to 40 C:N, which is more than double the maximum organic carbon to organic nitrogen ratio found for many of the samples in core JT96-06. While the ratios for the most part indicate that organic matter is marine in origin, these higher organic carbon to organic ratios are within the range of organic carbon to nitrogen ratios found for terrestrial derived organic matter. Although, considering studies by Wu et al. (1999) and McKay (2003), very little terrigenous organic matter travels beyond the coastal fjord system of Vancouver Island, furthermore there has been no evidence reported of inorganic and or organic sediment originating from the Strait of Jaun de Fuca, nor from further south, the Columbia River, has been transported to the shelf or slope along the southwest coast of Vancouver Island. Thus, it is more likely that increases in organic carbon to organic nitrogen ratios are the result of denitrification. In addition, the organic carbon to organic nitrogen ratios increase from core JT96-06, 620 m, to core JT96-07, 1170m, (Figure 5) which is likely the result of the organic matter traveling through the low oxygen, denitrifying, layer in the water column longer therefore causing increased nitrogen loss for samples from core JT96-07.

The $\delta^{13}\text{C}$ of settling particulate organic matter off Vancouver Island has an annual flux weighted average of -21.9‰ and can range from -23.0‰ to -20.6‰ (Wu et al., 1999; Mckay, 2003), $\delta^{13}\text{C}$ for other study sites along the west coast of Vancouver Island range from -23.4‰ to -21.2‰ (Pena et al., 1999). The $\delta^{13}\text{C}$ values for core JT96-06 range from -21.0‰ to -23.6‰ (Figure 9) for the Holocene portion of the core (Mckay, 2003), which is within the accepted range for marine derived organic matter (Figure 10) (Yen, 1975; Pedersen et al., 1992). McKay (2003) found that, although during the late

glacial and deglacial periods (prior to 13.5 kyr B.P. until about 11.2 kyr B.P.) 50 to 70% and 20 to 40% of the organic matter, respectively, was terrigenous, though the terrigenous contribution of organic matter to the shelf and slope in the Holocene was only a few percent. This compares with more than 50% terrigenous organic matter on the continental shelf off the coast of Washington State and 20 to 30% on the continental slope during the same time period (Pena et al., 1999; Mckay, 2003).

Surface Area

Bulk sediment surface areas for the study region are typical of continental shelf and slope sediments (Keil et al., 1994b; Mayer, 1994a; Mayer, 1994b; Hedges and Keil, 1995a; Cowie et al., 1999). Stratigraphic variability amongst the surface area data is similar to that found for both organic carbon and nitrogen, the variability ranges from 7 m²/g for core JT96-06 and 12 m²/g for JT96-07. The likely cause of the heterogeneity with respect to surface area is redistribution of sediments as a result of bottom water currents re-suspending and transporting the sediment elsewhere along the shelf and slope.

Surface Area–Organic Carbon Relationship

There is very poor correlation between organic carbon and surface area in both cores. Relatively, core JT96-06 shows a greater correlation than core JT96-07 (Figure 7 and Figure 8). The lack of a strong correlation between organic carbon and sediment surface area in these cores, when compared with studies by Bishop et al. (1992), Keil et al. (1994b), Mayer (1994a), Mayer (1994b), Hedges and Keil (1995a), Ransom et al (1997), Keil and Cowie (1999), Kaiser and Guggenberger (2000), Adams and Bustin

(2001), and Arnarson and Keil (2001), suggests that adsorption onto mineral surfaces is not a key factor in preserving organic matter in this region.

The majority of modern Holocene sediment distributed to the ocean gets trapped in the coastal fjord system of Vancouver Island, little modern inorganic sediment is being distributed to the continental shelf and slope, therefore the bulk of the Holocene inorganic sediment deposits that currently veneers the continental shelf and slope are likely relict deposits (Bornhold and Barrie, 1991). As there is modest distribution of recent inorganic sedimentary deposits beyond the coastal fjord system, there is less of a probability of mineral-organic particle interaction occurring in the water column than there would be in a coastal system with equal amounts of organic matter production and greater sediment distribution to the continental shelf and slope. The sediments that currently veneer the continental slope and shelf undergo re-suspension and re-distribution. During re-suspension and re-distribution of the sediment the adsorbed organic matter is being exposed to conditions that may be suitable for microbial attack of any loosely bound organic matter. Furthermore, the sediment is mixed and, therefore, dilution of sediment associated with organic matter by sediment with low surface area and little association with organic matter could be occurring. The lack of organic matter mineral interaction as well as dilution could be responsible for the observed poor correlation between organic matter and sediment surface area, however the lack of correlation could result from other mechanisms, other than adsorption protection, acting to preserve organic matter.

Conclusions

The continental slope along the southwestern coast of Vancouver Island shows no evidence that organic matter preservation is as result of adsorption onto sediment surfaces. There is a possibility that specific size fractions of the sediment may play a role in preserving organic matter, yet no relationship between organic carbon concentration and bulk sediment surface area is found for this region. Further investigations comparing the surface area and organic carbon concentration of various size fractions may prove to be prudent to determine if any association can be made between surface area and organic matter.

The stratigraphic variability of organic carbon concentrations, organic nitrogen concentrations, and $\delta^{13}\text{C}$ for this region are indicative of sediment redistribution along the continental slope. Thus the lack of correlation between bulk sediment surface area and organic carbon concentrations could be attributed to the movement of sediment from other regions along the continental shelf and slope.

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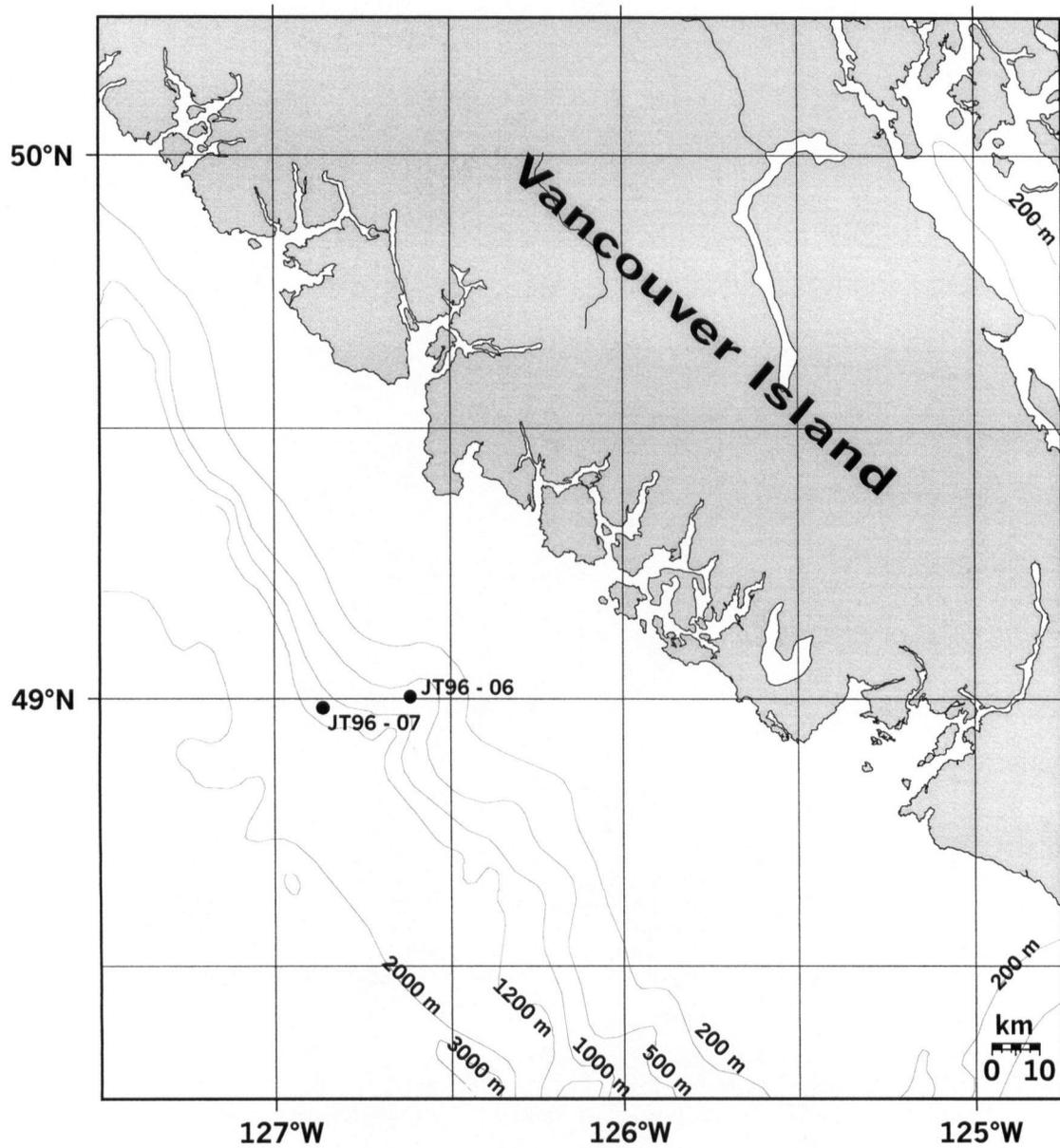


Figure 1: The study area is located along the west coast of Vancouver Island, British Columbia, Canada in the northeastern Pacific Ocean. Sediment cores were collected at core sites JT96-06 and JT96-07, at water depths of 620 m and 1170 m respectively.

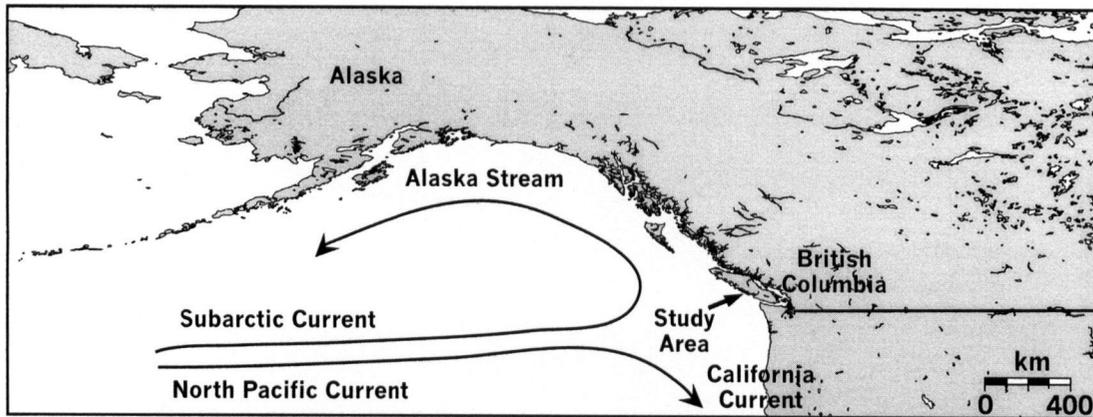


Figure 2: The study area is affected by the Subarctic Current, North Pacific Current and the California Current.

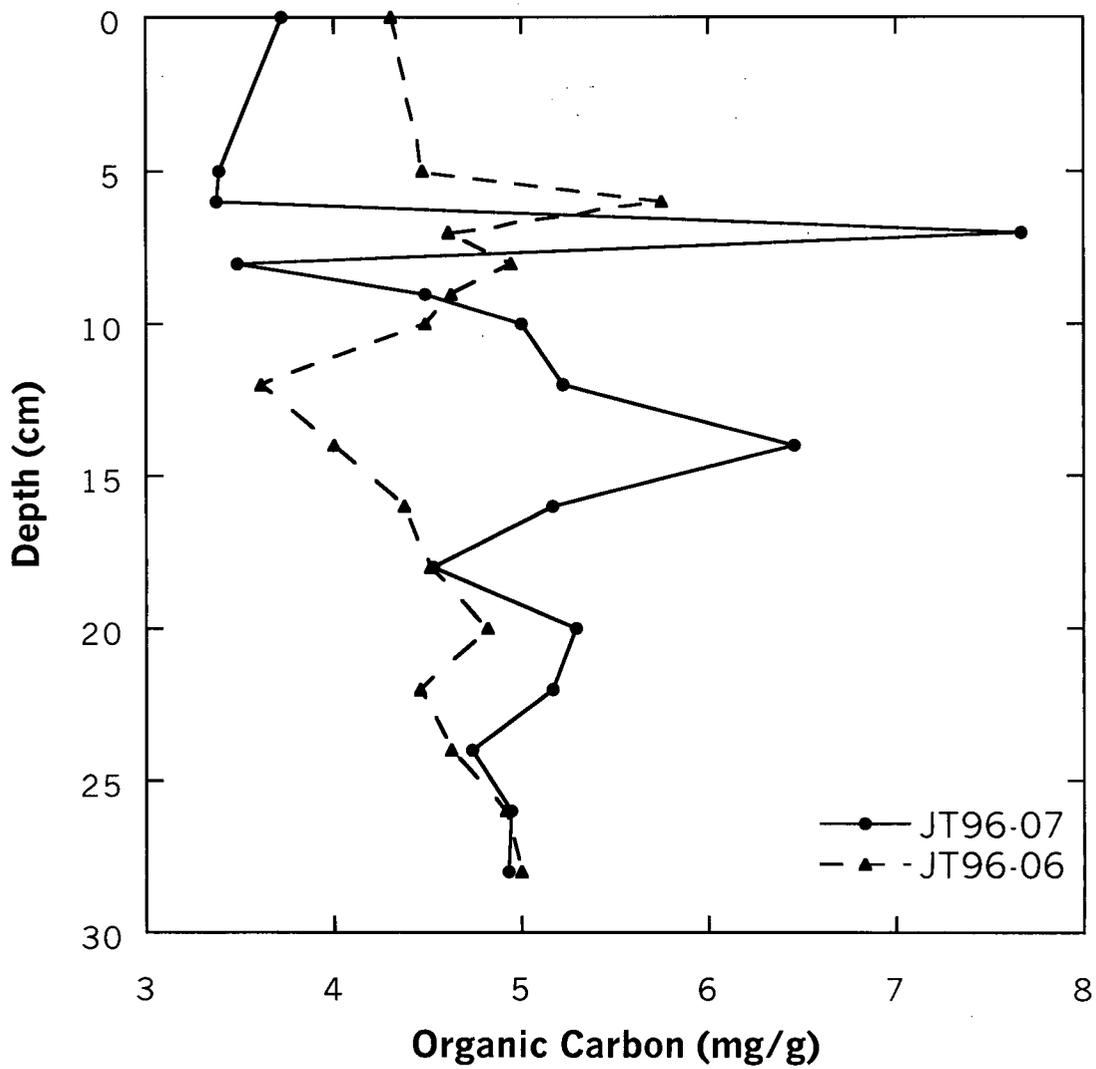


Figure 3: Concentrations of organic carbon in the near surface sediments of cores JT96-06 and JT96-07.

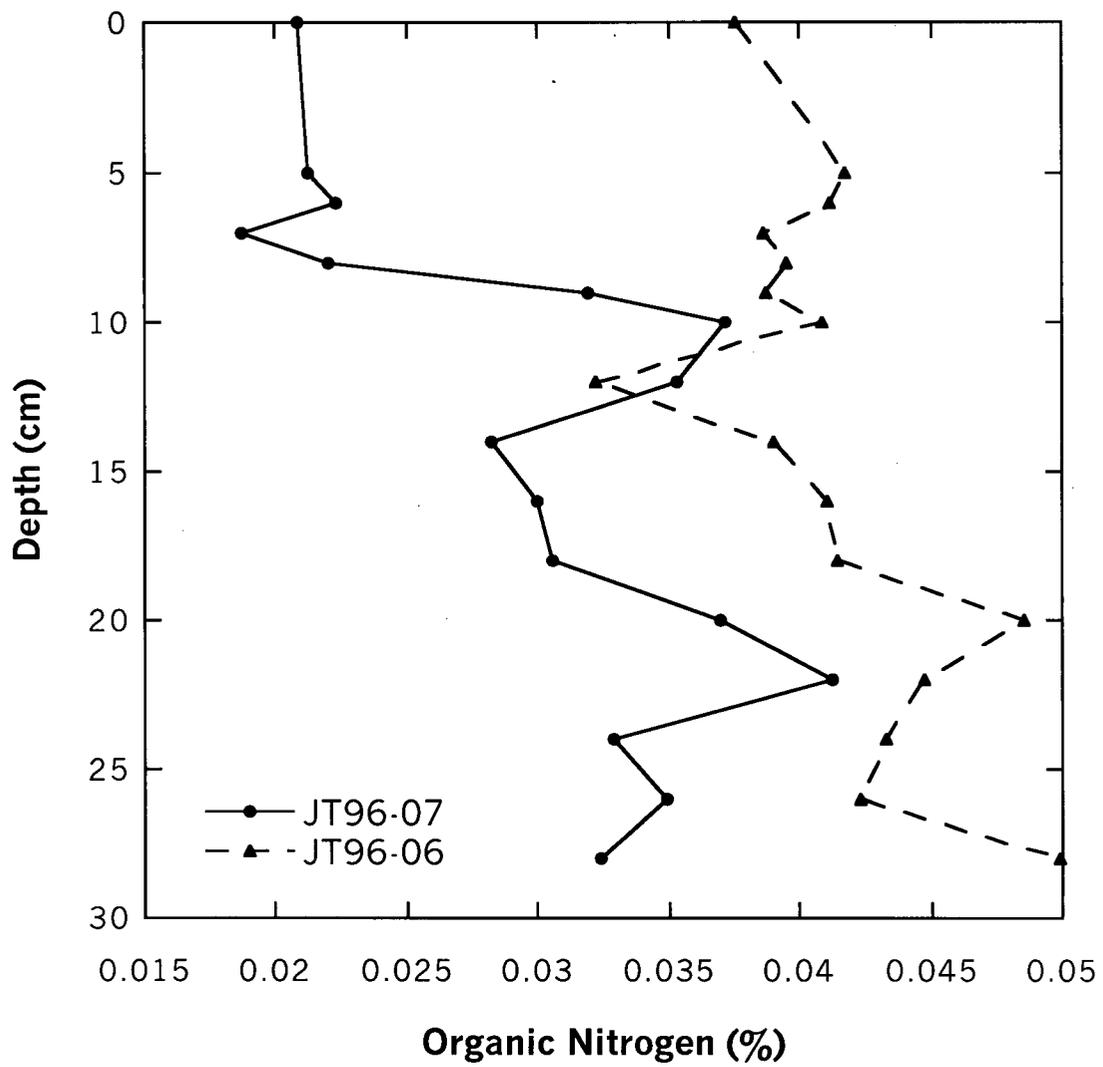


Figure 4: Concentration of organic nitrogen in the near surface sediments of cores JT96-06 and JT96-07.

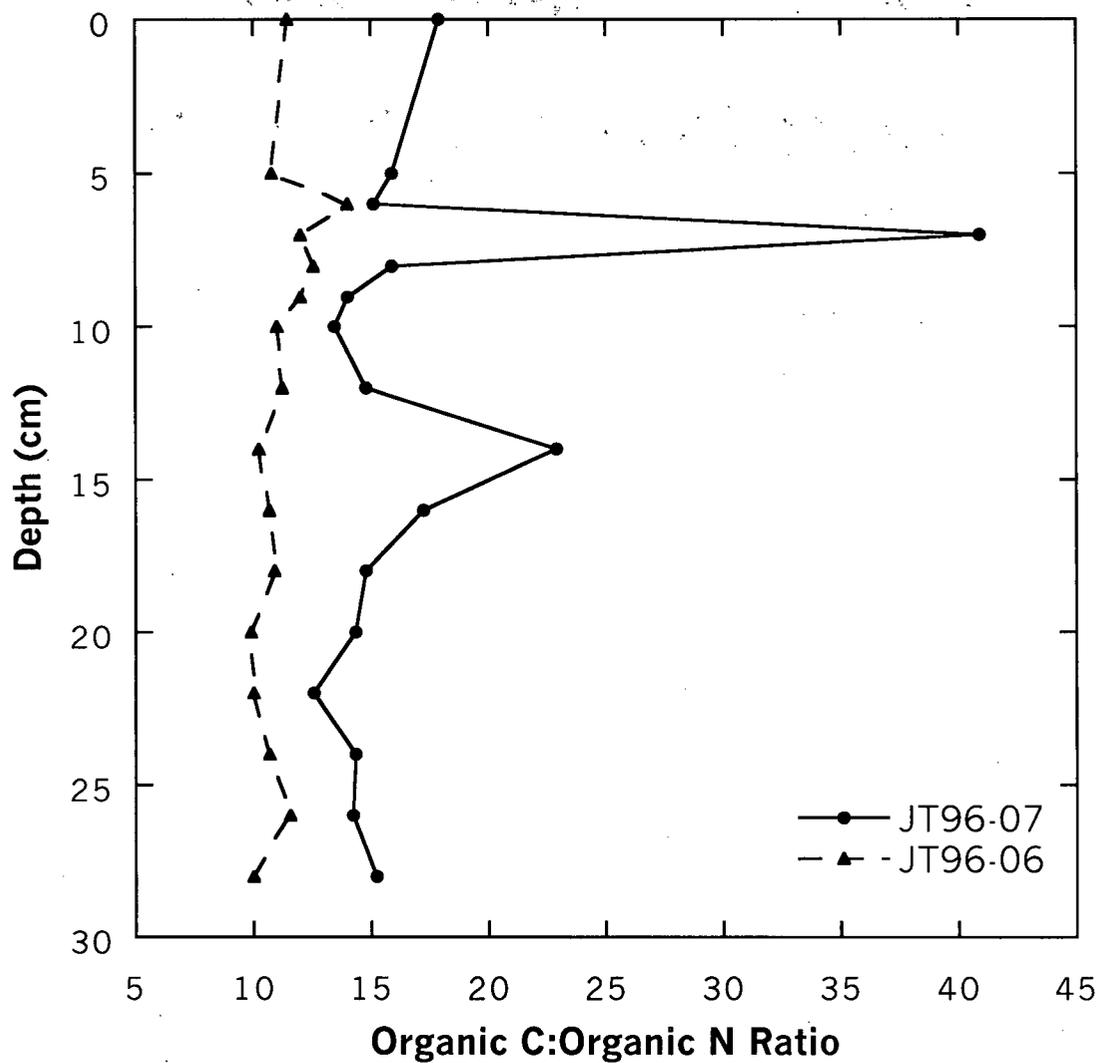


Figure 5: Stratigraphic profile of the organic carbon to organic nitrogen ratios for cores JT96-06 and JT96-07.

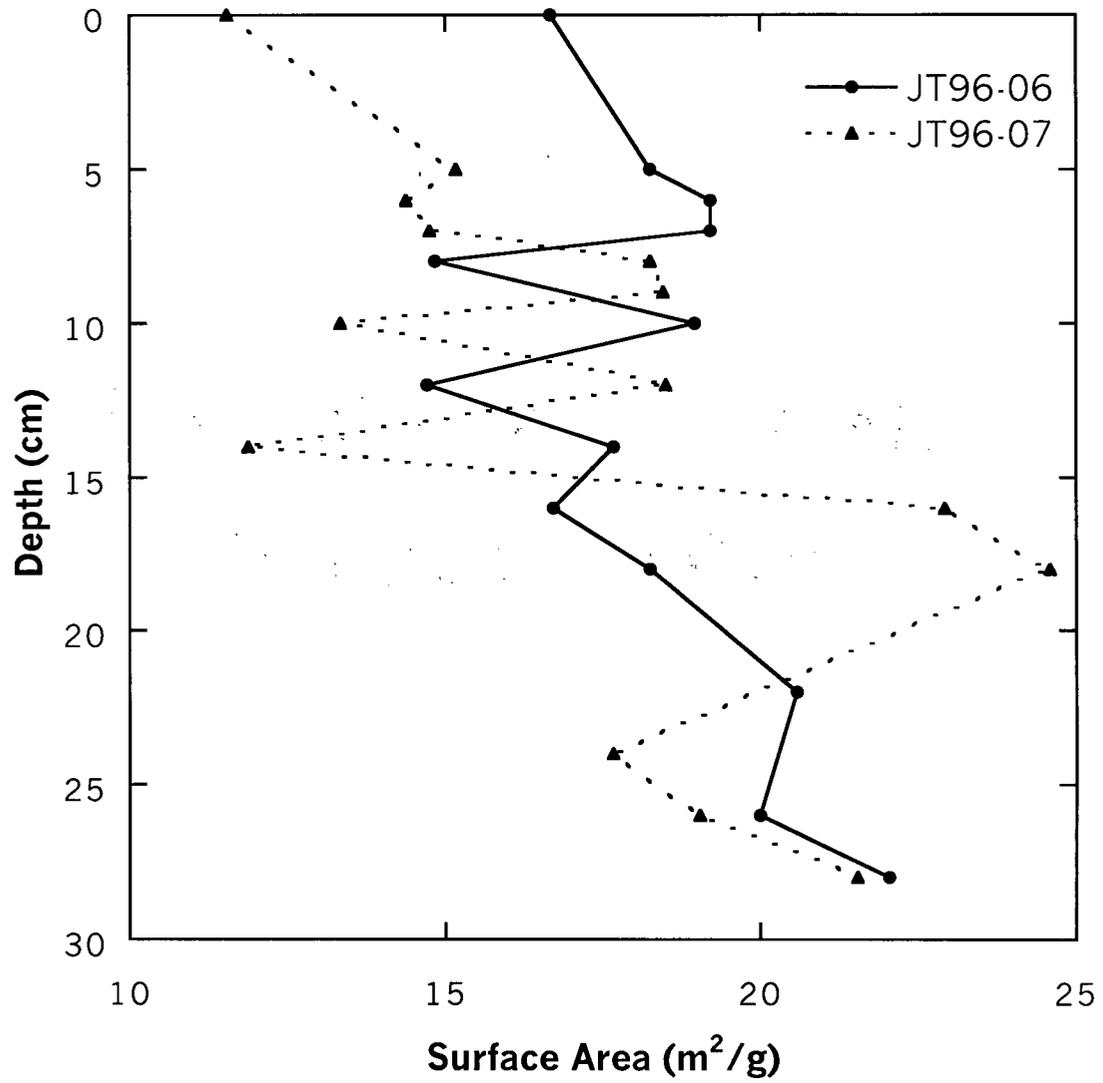


Figure 6: Stratigraphic profile of bulk sediment surface area values for cores JT96-06 and JT96-07.

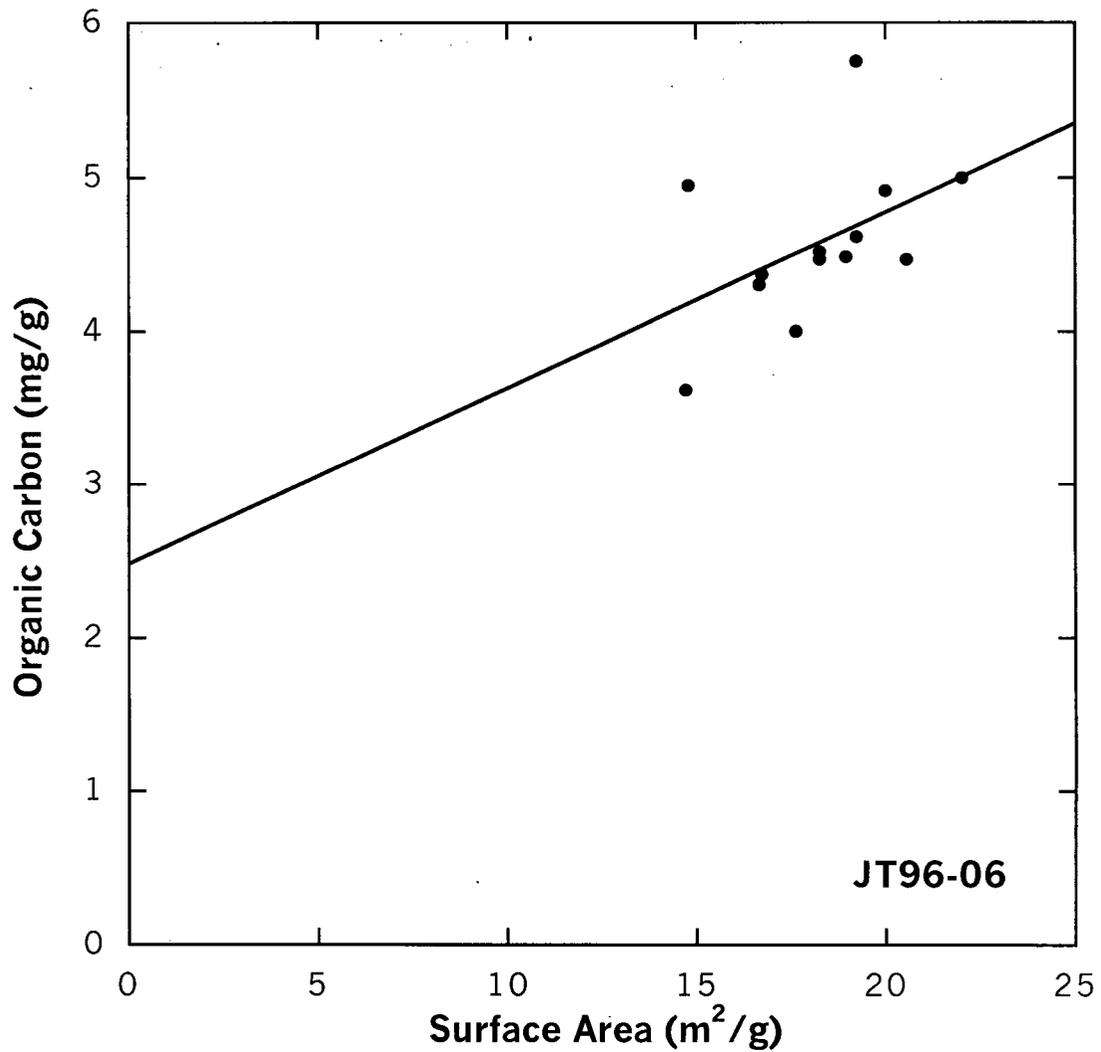


Figure 7: Comparison of organic carbon concentrations and bulk sediment surface area for core JT96-06. The correlation coefficient for the relationship between organic carbon concentration and bulk sediment surface area is 0.47, meaning that there is a moderate correlation between the two variables.

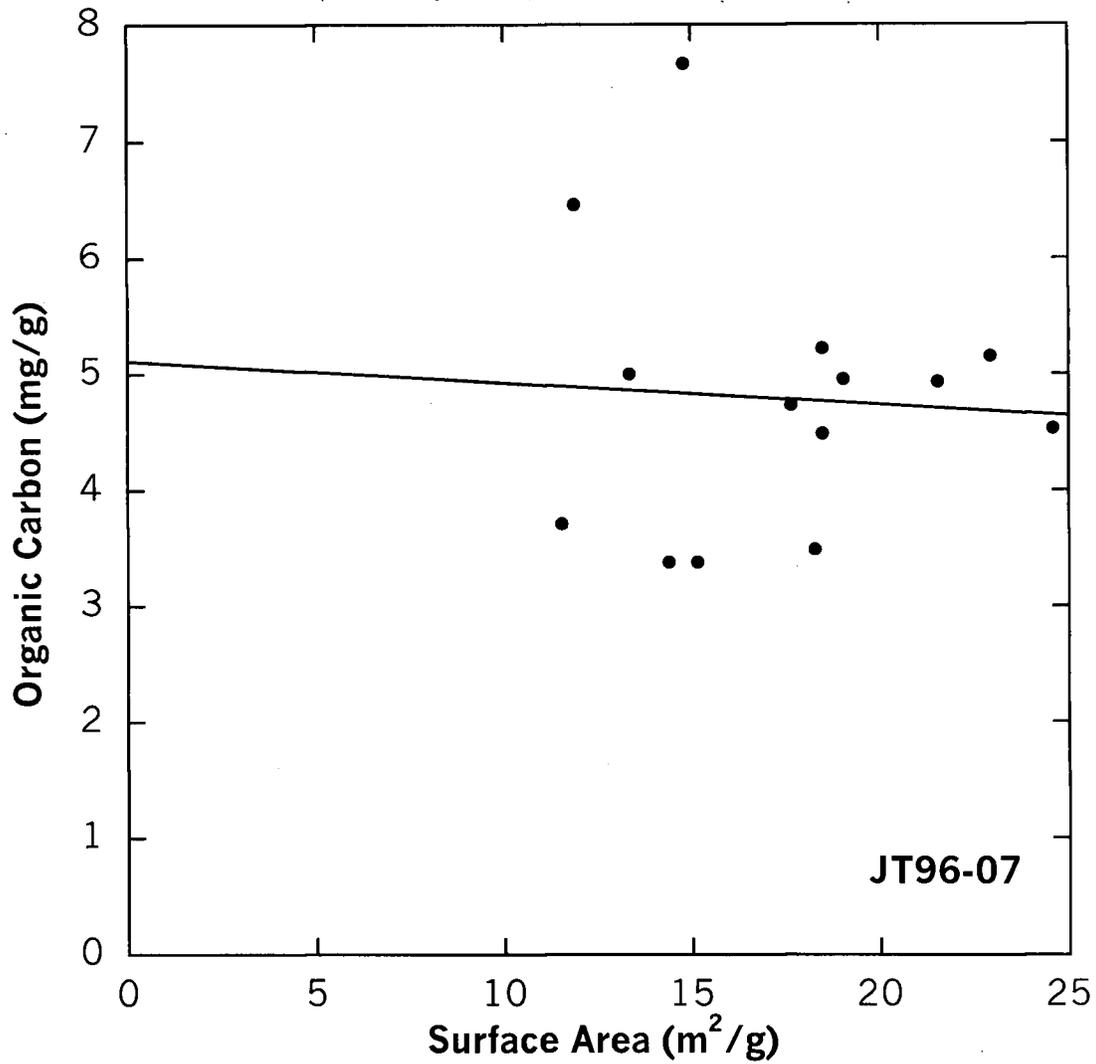


Figure 8: Comparison of organic carbon concentrations and bulk sediment surface area for core JT96-07. The correlation coefficient between the two variables is -0.063 indicating a poor relationship between organic carbon and bulk sediment surface area.

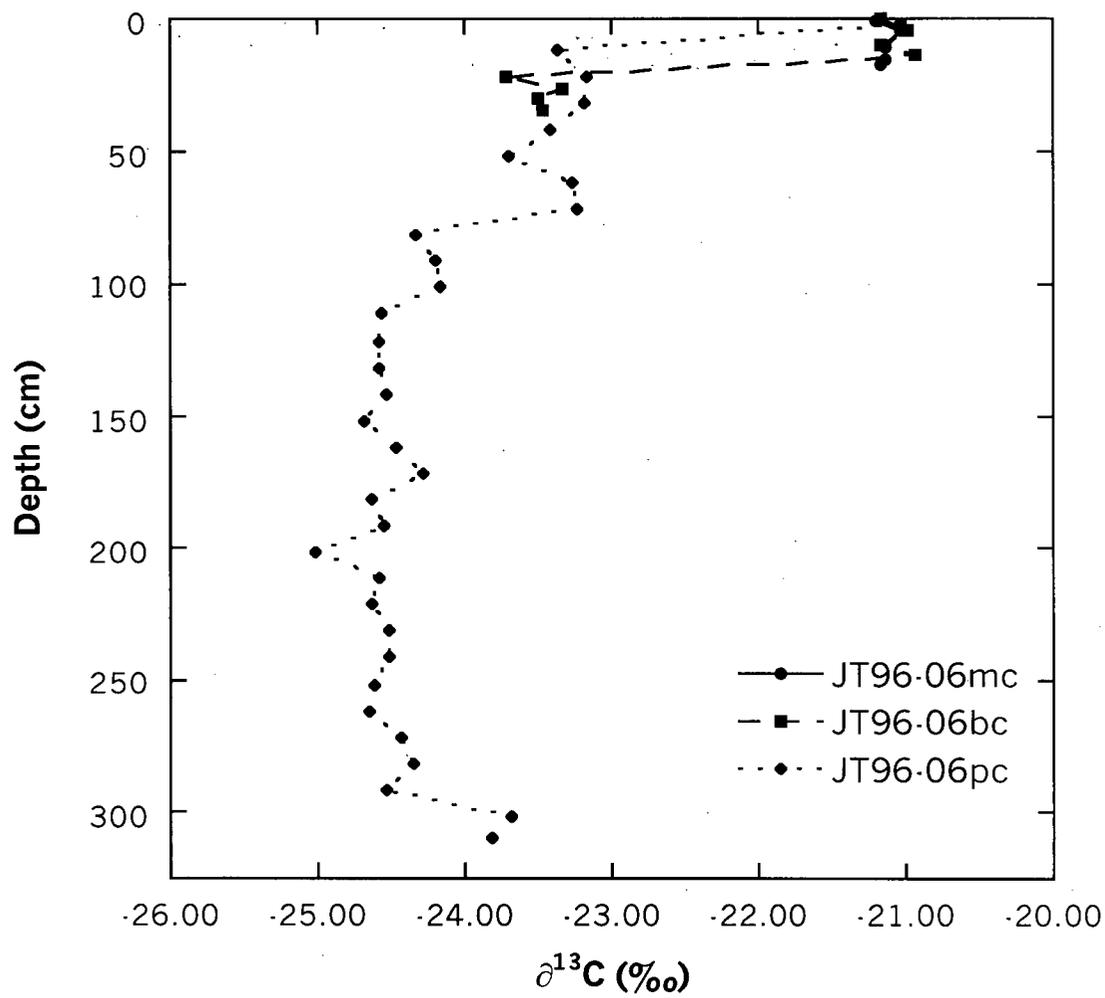


Figure 9: $\delta^{13}\text{C}$ values for box core (JT96-06bc), multi-core (JT96-06mc) and piston core (JT96-06pc) samples at sample site JT96-06. Data from McKay (2003).

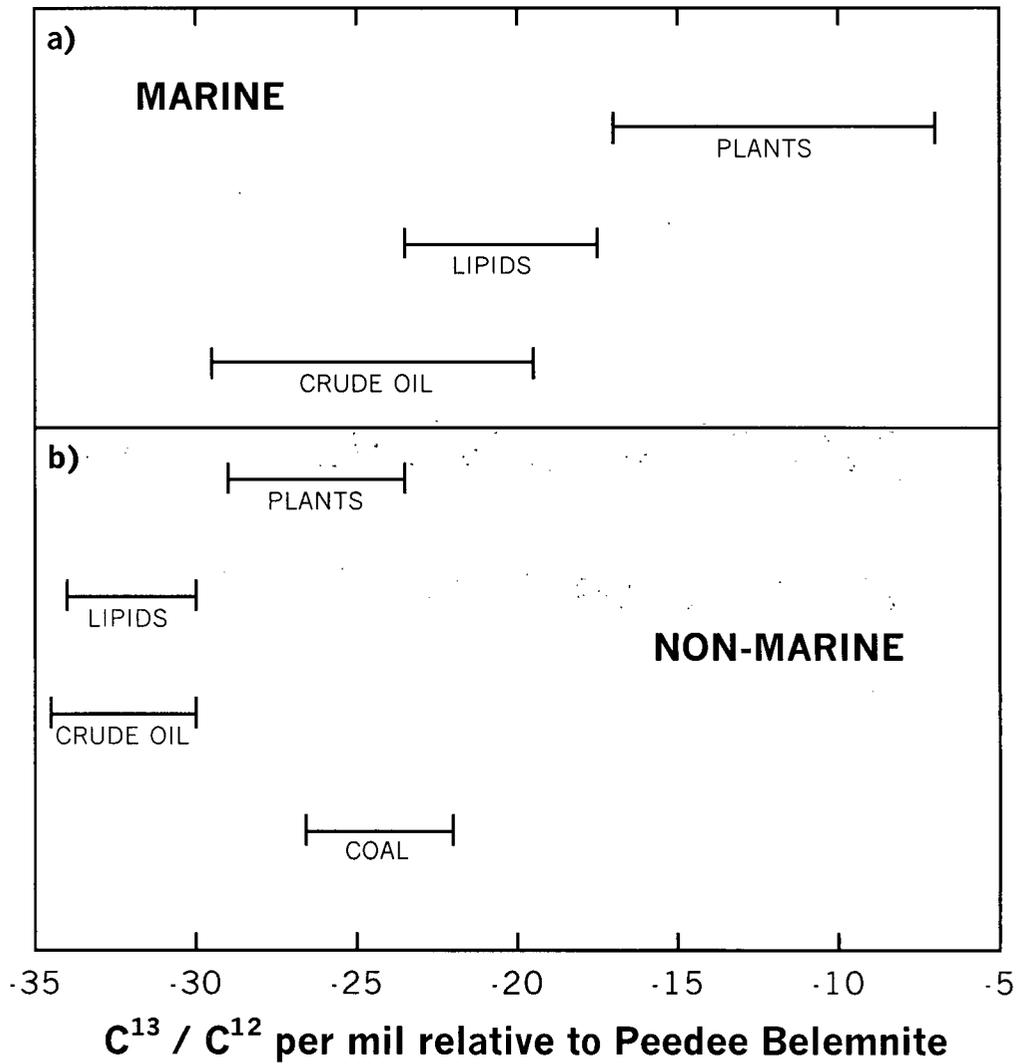


Figure 10: Carbon isotope range of natural materials, a) Marine derived organic matter and b) Non-marine, or terrestrial, derived organic matter. After Yen (1975).

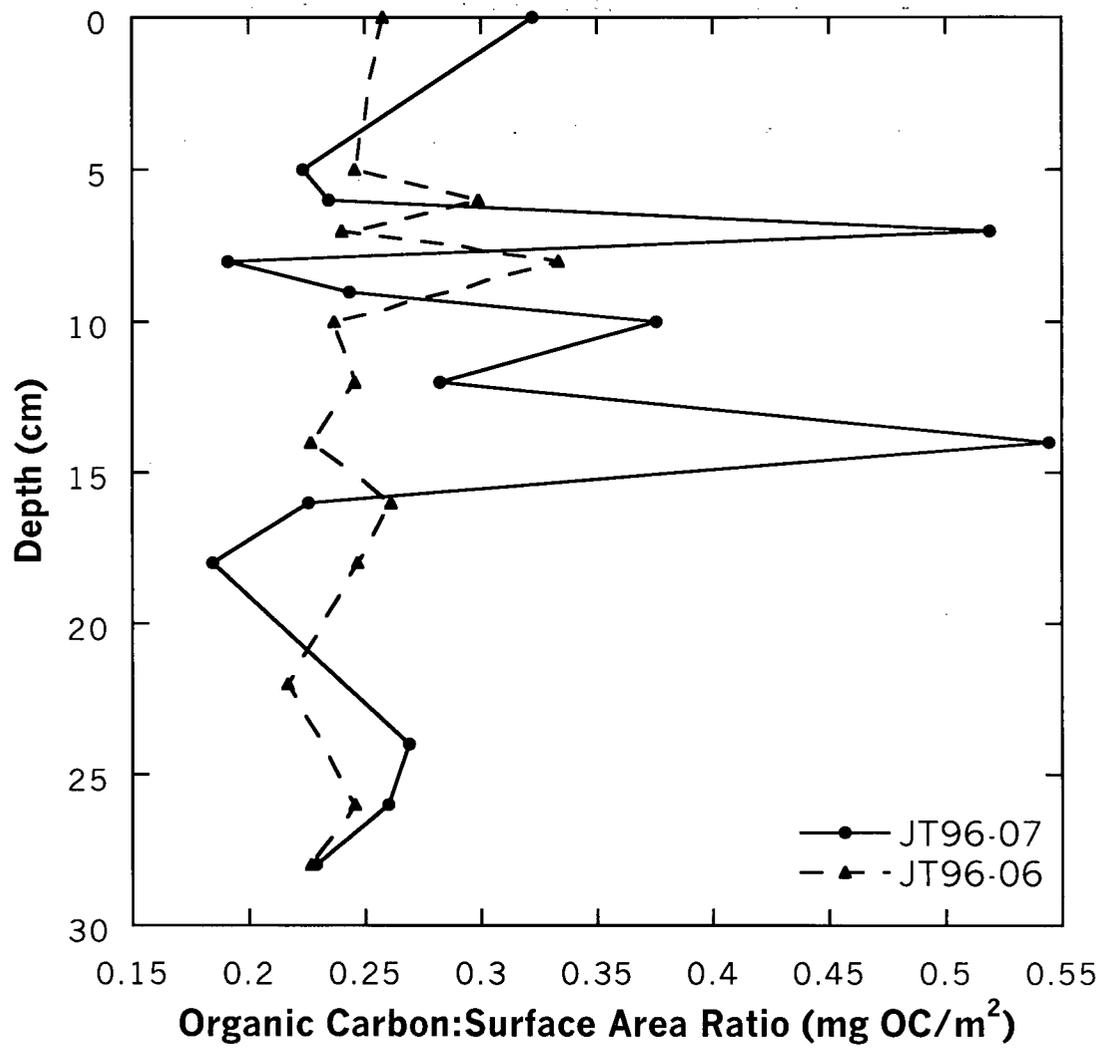


Figure 11: Stratigraphic profile of the organic carbon concentration to bulk sediment surface area ratios for cores JT96-06 and JT96-07.

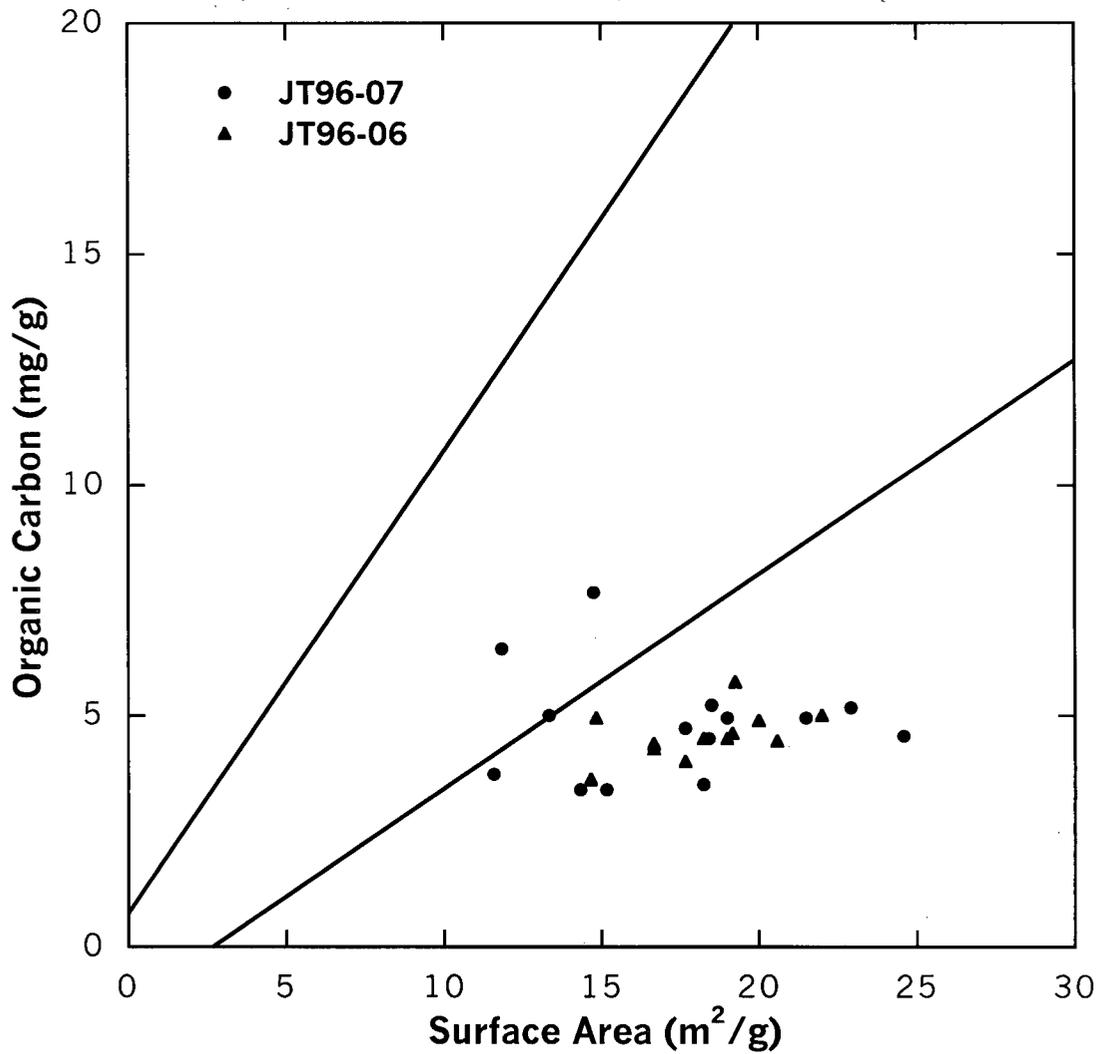


Figure 12: Comparison of organic carbon concentration and bulk sediment surface area for both core JT96-06 and core JT96-07, the area between the two solid lines is the monolayer equivalence level, as determined by Mayer (1994ab).

Table 1: Bulk sediment surface area, SA, total carbon, TC, inorganic carbon, IOC, organic carbon, OC, total nitrogen, TN, organic nitrogen, ON, organic carbon to organic nitrogen ratio, OC/ON, and organic carbon to surface area ratio, OC/SA for cores JT96-06 and JT96-07 from the continental slope of Vancouver Island.

Core: JT96-06

Depth (cm)	SA (m ² /g)	TC (%)	IOC (%)	OC (%)	OC (mg/g)	TN (%)	ON (%)	OC/ON	OC/SA (mg/m ²)
0	16.67	0.53	0.10	0.43	4.30	0.041	0.038	11.46	0.26
5	18.26	0.53	0.08	0.45	4.48	0.045	0.042	10.73	0.25
6	19.22	0.66	0.09	0.57	5.75	0.044	0.041	13.97	0.30
7	19.21	0.52	0.06	0.46	4.62	0.042	0.039	11.96	0.24
8	14.82	0.52	0.03	0.49	4.95	0.042	0.039	12.52	0.33
9	18.35	0.53	0.07	0.46	4.63	0.042	0.039	11.97	0.25
10	18.98	0.55	0.10	0.45	4.49	0.044	0.041	10.99	0.24
12	14.70	0.43	0.07	0.36	3.61	0.035	0.032	11.22	0.25
14	17.67	0.50	0.10	0.40	4.00	0.042	0.039	10.24	0.23
16	16.71	0.51	0.07	0.44	4.37	0.044	0.041	10.64	0.26
18	18.25	0.53	0.08	0.45	4.51	0.044	0.041	10.88	0.25
20	19.51	0.54	0.06	0.48	4.82	0.052	0.049	9.93	0.25
22	20.57	0.54	0.09	0.45	4.46	0.048	0.045	9.97	0.22
24	20.15	0.53	0.07	0.46	4.62	0.046	0.043	10.68	0.23
26	19.99	0.56	0.07	0.49	4.91	0.045	0.042	11.60	0.25
28	22.03	0.59	0.09	0.50	5.00	0.053	0.050	10.01	0.23
Average:	18.44	0.54	0.08	0.46	4.59	0.044	0.041	11.17	0.25

Table 1: (continued)

Core: JT96-07

Depth (cm)	SA (m2/g)	TC (%)	IOC (%)	OC (%)	OC (mg/g)	TN (%)	ON (%)	OC/ON	OC/SA (mg/m2)
0	11.55	0.60	0.23	0.37	3.72	0.040	0.021	17.88	0.32
5	15.17	0.59	0.25	0.34	3.38	0.040	0.021	15.94	0.22
6	14.36	0.59	0.25	0.34	3.37	0.041	0.022	15.11	0.23
7	14.77	1.03	0.26	0.77	7.66	0.037	0.019	40.94	0.52
8	18.25	0.66	0.31	0.35	3.49	0.041	0.022	15.85	0.19
9	18.46	0.70	0.25	0.45	4.48	0.051	0.032	14.05	0.24
10	13.33	0.72	0.22	0.50	5.00	0.056	0.037	13.46	0.38
12	18.48	0.73	0.21	0.52	5.23	0.054	0.035	14.79	0.28
14	11.87	0.85	0.20	0.65	6.46	0.047	0.028	22.87	0.54
16	22.93	0.72	0.20	0.52	5.16	0.049	0.030	17.22	0.23
18	24.60	0.67	0.22	0.45	4.53	0.049	0.031	14.84	0.18
20	21.52	0.74	0.21	0.53	5.29	0.056	0.037	14.31	0.25
22	20.52	0.74	0.22	0.52	5.17	0.060	0.041	12.54	0.25
24	17.65	0.67	0.20	0.47	4.74	0.052	0.033	14.39	0.27
26	19.03	0.69	0.20	0.49	4.95	0.054	0.035	14.18	0.26
28	21.54	0.67	0.18	0.49	4.93	0.051	0.032	15.20	0.23
Average:	17.75	0.71	0.23	0.48	4.85	0.048	0.030	17.10	0.29

Table 2: $\delta^{13}\text{C}$ data for core JT96-06, data is reported for three different core types: box core, multi-core and piston core. Data from McKay (2003).

Core: JT96-06

Core Type	Depth (cm)	$\delta^{13}\text{C}$
Box Core	0.3	-21.17
	4.5	-20.99
	10.0	-21.16
	14.0	-20.94
	22.0	-23.71
	26.0	-23.33
	30.0	-23.50
	34.0	-23.46
Multi-core	1.0	-21.20
	5.0	-21.03
	11.0	-21.14
	15.0	-21.13
	17.0	-21.16
Piston Core	1.5	-21.04
	11.5	-23.36
	21.5	-23.17
	31.5	-23.19
	41.5	-23.41
	51.5	-23.70
	61.5	-23.27
	71.5	-23.23
	81.5	-24.33
	91.5	-24.20
	101.5	-24.16
	111.5	-24.56
	121.5	-24.58
	131.5	-24.58
	141.5	-24.53
	151.5	-24.68
	161.5	-24.46
	171.5	-24.28
	181.5	-24.63
	191.5	-24.55
201.5	-25.02	
211.5	-24.59	
221.5	-24.63	
231.5	-24.51	
241.5	-24.52	
251.5	-24.61	
261.5	-24.65	
271.5	-24.44	
281.5	-24.35	
291.5	-24.54	
301.5	-23.69	
309.5	-23.81	

Chapter 3 - Surface area control on organic matter preservation in the Makran area of the Arabian Sea

Abstract

Samples from the continental shelf and slope along the coast of Pakistan, in the Makran area of the Arabian Sea, have been analyzed to determine the global applicability of the recent theory of adsorption protection of organic matter onto sediment surfaces, as well the notion of monolayer coverage of sediment by organic matter has also been tested. The Makran area of the Arabian Sea undergoes seasonal primary production on the order of $200 - 400 \text{ g C m}^{-2} \text{ year}^{-1}$, whilst the inorganic sedimentary input from riverine and aeolian sources provide sedimentation rates of greater than 150 cm/kyr . The concentration of organic matter along the continental shelf and slope beneath this highly productive region ranges from $0.50 - 2.48\%$. Bulk sediment surface area for the Makran area ranges from $10.0 - 24.8 \text{ m}^2/\text{g}$. While a considerable amount of organic matter is preserved along the continental slope of the Makran area, there is no relationship between sediment surface area and organic carbon concentration, therefore the sediment surfaces are not acting to enhance organic matter preservation for this region. Furthermore, from the fractional coverage calculations used the organic matter that had been associated with the sediment surfaces appears to be covering $<22\%$ of the total surface of a given sediment grain, thus dispelling the notion that organic matter covers the entire surface of a sediment grain in monolayer coating.

Introduction

Marine sediments play an important role in the global carbon cycle; they are used as environmental indicators and are an important source for fossil fuels. Sedimentary organic matter provides information on the provenance, depositional history, and resource potential of marine sediments. However, an incomplete understanding of the factors that control the content and preservation of organic matter in marine sediments complicate many investigations (Keil et al., 1994b). Organic matter preserved in marine sediments accounts for approximately 1% of the total organic matter produced and/or supplied to the surface ocean (Suess, 1980; Hedges and Keil, 1995a). Phytoplankton photosynthesis accounts for approximately 50 Gt yr⁻¹ of organic carbon (Siegenthaler and Sarmiento, 1993), as the phytoplankton die they become efficiently recycled throughout the ocean water column (Hedges et al., 1997); 10% of the total organic matter produced in the surface ocean is exported to the deep ocean where 90% is oxidized before it reaches the sea floor (Hedges and Keil, 1995a). When considering the minimal amount of organic matter that reaches the sea floor, understanding the mechanisms by which organic matter is preserved is important in understanding the distribution of petroleum source rocks (Adams and Bustin, 2001).

Previous studies that have investigated the relationship between organic matter preservation and local oceanographic conditions have yielded mixed results (Keil and Cowie, 1999). Until the 1990s, the predominant view was that organic matter accumulation was primarily the result of anoxic bottom water slowing the decay of

organic matter leading to enhanced organic matter preservation (Demaison and Moore, 1980). Although data for many regions do show increased organic matter preservation in sub-oxic to anoxic regions, this theory does not fully account for organic matter accumulation in oxygen rich regions, such as along continental shelves, outside the oxygen minimum zone (Calvert et al., 1992; Pedersen et al., 1992; Calvert and Pedersen, 1993; Calvert et al., 1995; Ganeshram et al., 1999). Additionally, during the last glacial maximum, in some regions, an appreciable amount of organic matter accumulated even though the bottom waters and uppermost sediment column remained oxic (Calvert and Pedersen, 1993) and in some basins decomposition of organic matter under anoxic conditions has been shown to occur at rates comparable to those under oxic conditions (Canfield, 1989).

The observation that enhanced organic matter preservation can occur regardless of the redox conditions in the water-column and within the sediment implies that other organic matter preservation mechanisms must be important. There are a number of controlling factors that have been proposed including: 1.) sedimentation rates (Demaison and Moore, 1980; Calvert et al., 1992); 2.) the rate of organic matter production in the overlying water column (Calvert et al., 1992; Pedersen et al., 1992; Calvert and Pedersen, 1993; Calvert et al., 1995; Bergamaschi et al., 1997); 3.) inorganic and organic sediment sources (Weiler and Mills, 1965; Demaison and Moore, 1980; Hedges et al., 1997); and 4.) sediment surface area (Weiler and Mills, 1965; Keil et al., 1994b; Mayer, 1994a; Mayer, 1994b; Hedges and Keil, 1995a; Cowie et al., 1999).

Sedimentation rate has been suggested as being a primary control on organic matter preservation, irrespective of bottom-water oxygen concentrations (Muller and Suess, 1979; Canfield, 1989; Calvert et al., 1992; Pedersen et al., 1992). Regardless of the amount of organic matter being produced in surface waters, if the sediment input to a highly productive region is high then the amount of organic matter within the deposited sediments becomes diluted. In the rock record this diluted organic matter concentration may be initially confused with low organic matter production, or possibly low preservation. Conversely, if sediment input were low then organic matter in the underlying marine sediments would appear organic rich. Although, when sediment input to the sea floor is low there is a greater chance that the organic matter will undergo microbial degradation.

The rate of organic matter production in the surface ocean has been suggested as a secondary mechanism that can yield high organic matter concentrations in marine sediments (Calvert et al., 1995). The concept of high organic matter input begets high organic matter preservation has been utilized to discredit the classic theory of low bottom-water oxygen concentration alone increases the potential for enhanced organic matter preservation. In upwelling regions, such as off the coast of Peru, high rates of primary production give rise to greater than average export of organic matter from the surface ocean, which thereby increases the concentration of organic matter in the underlying sediments. In low productivity regions, such as within the Sargasso Sea, the amount of organic matter preserved in the underlying sediment is much less than off

Peru, therefore indicating that for high organic matter preservation in the sediments high productivity in the overlying water column would be of key importance.

Over the past couple of decades, several investigators have found a relationship between grain size and organic matter concentration. Recently, studies have further investigated the concept of organic matter preservation controlled by sediment surface area, the “adsorption protection theory.” In many regions worldwide there are correlations between the surface area of sediment grains and the amount of organic matter preserved in the sediment (Keil et al., 1994b; Mayer, 1994a; Mayer, 1994b; Hedges and Keil, 1995a; Ransom et al., 1997; Cowie et al., 1999). The introduction of the adsorption protection theory has further clarified qualitative observation in previous studies; however, as to whether adsorption protection holds the key to understanding organic matter preservation in general still remains unknown.

The Arabian Sea provides an exceptional opportunity to evaluate the mechanism that aid and/or enhance organic matter preservation in a region that has high primary productivity and a moderate sediment input. This study examines sediments from the northern Arabian Sea to determine the applicability of the adsorption protection theory for this region and evaluates the role adsorption of organic matter plays on preservation with respect to other known preservation mechanisms.

Background

Arabian Sea

The study region is the Makran area in the Arabian Sea, located along the Pakistani continental slope and shelf (Figure 1). Four major seasons exist in the Arabian Sea: (1) spring intermonsoonal; (2) southwest monsoon; (3) fall intermonsoonal; and (4) northeast monsoon season (Latasa and Bidigare, 1998; Smith et al., 1998b). The southwest and northeast monsoonal events are important for primary production. The southwest monsoonal event gives rise to wind mixing of the water column causing destratification and upwelling of deep nutrient rich water towards the surface (Borole, 2002). The northeast monsoonal event creates convective mixing of the waters in the Arabian Sea and, much like during the southwest monsoonal event, nutrients are mixed throughout the water column (Borole, 2002). Primary production during the northeast monsoonal season is generally low with the exception of some regions along the coast of Pakistan (Wyrтки, 1973; Reichart et al., 1997). During the southwest monsoonal season, coastal upwelling along Oman and open ocean upwelling in the Arabian Sea drive primary production rates that are amongst the highest known for the open ocean (Reichart et al., 1997). Annual productivity rates for the Arabian Sea range from 200-400 g C m⁻² year⁻¹ (Reichart et al., 1997; Smith et al., 1998a). The result of the monsoonal events are seasonally and spatially variable upwelling and dust inputs, which lead to increased micro- and macro- nutrients giving rise to high primary production (Cowie et al., 1999). The variability in upwelling and dust input lead to pulses of primary production, which in turn create pulses of particulate organic matter flux to the sea floor (Cowie et al., 1999),

with organic carbon and nitrogen concentrations reaching their maximum between 200 and 1600 m water depth (Calvert et al., 1995).

Between 200 and 800 m water depth, the water column in the northern and northeastern Arabian Sea is depleted with respect to oxygen (Calvert et al., 1995). The oxygen minimum zone is the result of the input of low oxygen intermediate waters from the western boundary of the Arabian Sea along with intense microbial remineralization of organic matter depleting any available oxygen (Cowie et al., 1999; Staubwasser and Sirocko, 2001). Intermediate bottom water is supplied to the Pakistani continental shelf and slope by way of the Somalia current (Staubwasser and Sirocko, 2001). In transport, the water becomes depleted of its oxygen via organic matter remineralization as the water passes under the highly productive surface waters along the Somalia and Oman coasts (Staubwasser and Sirocko, 2001). As currents carry the intermediate water to the north and east, nitrate reduction becomes the dominating respiratory process in microbial consumption of organic matter (Staubwasser and Sirocko, 2001 and references therein).

The distribution of organic matter in the Arabian Sea has, thus far, been attributed to: 1) variations in supply, decreasing away from coastal upwelling centers and decreasing with increasing water depth; 2) the texture of sediments (coarser-grained sediments having lower organic carbon concentrations associated with them); 3) possible sediment-organic matter interactions; and by 4) dilution via other sedimentary components (Pedersen et al., 1992; Calvert et al., 1995; Cowie et al., 1999; Staubwasser and Sirocko, 2001). The distribution of organic matter is also affected by diagenetic

factors such as remineralization via microbial degradation during sedimentation and burial.

Sediment sources to the Makran area include riverine deposits, wind blown aeolian deposits, and re-deposition of sediments along the shelf and slope. The Indus River, Hab River and Hingol River supply riverine sedimentary deposits from Pakistan and India (Calvert et al., 1995; Staubwasser and Sirocko, 2001), while aeolian deposits are distributed to the Arabian Sea from the Thar Desert, Arabian Peninsula and The Iran-Makran area (Reichart et al., 1997; Borole, 2002). The Thar Desert, alone, contributes approximately 100 million tonnes of aeolian dust to the Arabian Sea annually (Borole, 2002). Re-distribution of sediment in the Makran area occurs through: monsoonal storm events carrying sediment along the continental shelf (Calvert et al., 1995; Staubwasser and Sirocko, 2001); turbidity currents that carry sediment along the shelf and down the slope (Calvert et al., 1995); as well as through the dewatering along thrust faults causing large-scale expulsion of mud on the shelf by mud volcanoes (Staubwasser and Sirocko, 2001). Sedimentation rates along the continental shelf and slope of India are on the order of 70-150 cm/kyr (0.7-1.5 mm/a), while sedimentation rates for the Makran area have been estimated to be greater than 150 cm/kyr (Staubwasser and Sirocko, 2001).

Adsorption Protection Theory

Adsorption protection of organic matter onto sediment particle surfaces has become increasingly invoked as a mechanism to explain preservation of organic matter along continental shelf and slope regions. Organic matter from marine and/or terrigenous

sources may be adsorbed onto sediment surfaces, either in the water column or within the sediment. Strong correlations between organic matter and sediment surface area has been shown by Bishop et al. (1992), Keil et al. (1994b), Mayer (1994a), Mayer (1994b), Hedges and Keil (1995a), Ransom et al (1997), Keil and Cowie (1999), Kaiser and Guggenberger (2000), Adams and Bustin (2001), and Aranarson and Keil (2001). As the surface area of the mineral grains increase so to does the concentration of organic matter (Mayer, 1994b).

There are conflicting views as to whether organic matter coats the entire surface of the mineral grain (Ransom et al., 1997), or adsorbed into intragranular mesopores (2 to 50 nm) and micropores (< 2 nm) (Mayer, 1994a; Mayer, 1994b), or lays in intergranular mesopores (Bock and Mayer, 2000). Ransom et al. (1997) propose that organic matter is adsorbed over discrete patches on the mineral surface, while Mayer (1994b) concluded alluminosilicate sediments and soils have mesopores and micropores, which might contribute to this discrete patchiness. More recently, Bock and Mayer (2000) have concluded that mesopores in the sediment, rather than on or within the sediment particles, act to protect organic matter provided the organic matter is positioned, with respect to the pore geometry, such that access via microbes and enzymes is restricted. If the organic matter is adsorbed into these pores, either on the sediment particle surface or on internal surfaces of the clay particles, then the organic matter is isolated from hydrolytic enzymes, which are responsible for the initial steps in organic matter decay, as these enzymes are too large to easily enter the pores the organic matter remains isolated (Mayer, 1994a).

Therefore, isolation from initial decay reduces the likelihood that the organic matter will be destroyed during diagenesis.

It has been proposed that organic matter is adsorbed as a discrete single layer covering the grains with a monolayer coating (Weiler and Mills, 1965; Mayer, 1994a; Mayer, 1994b). Complete coverage of a mineral grain is the monolayer equivalence level, or the concentration of organic carbon per square metre that covers the entire mineral surface (Mayer, 1994). The monolayer equivalence level should be considered a maximum coating potential of a mineral grain, and falls between 0.5 and 1.0 mg OC m⁻² (Mayer, 1994a; Mayer, 1994b).

Recently, there has been compelling evidence offered to suggest that organic matter does not necessarily coat the surface of each individual sediment and/or mineral grain in a single molecule thick layer, but more likely adsorbs onto high enthalpy adsorption sites in discrete patches (Mayer, 1999). The extent of coverage by organic matter on mineral surfaces is determined from the Brunauer-Emmett-Teller (BET) theory for surface area determination. BET theory defines a C constant variable that is related to enthalpies of gas adsorption onto a surface:

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

where M is a non-dimensional ratio which is indeterminate for most adsorbent-adsorbate system and is considered equal to 1; ΔH_{ads} is the adsorption enthalpy of gas on the surface; ΔH_{cond} is the enthalpy of gas condensation equivalent to adsorption of the second or higher layers of gas; ΔH_{xs} is the difference between ΔH_{ads} and ΔH_{cond} ; R is the universal gas constant; and T is the temperature in degrees Kelvin (Gregg and Sing, 1982; Mayer,

1999). Mayer (1999) used the relationship between the C constant and ΔH_{xs} to compare enthalpies of adsorption both prior to organic matter removal from the sediment and after organic matter removal to determine the fractional coverage of organic matter on mineral grains:

$$\Delta(\Delta H_{xs})_{\text{naked-coated}} = 4.19 (\text{Fractional coverage})^{0.535} \quad [2]$$

where $\Delta(\Delta H_{xs})_{\text{naked-coated}}$ is the difference in enthalpies of adsorption between samples without and with organic matter. Mayer (1999), Mayer and Xing (2001) and Mayer et al. (2002) determined that for a majority of the samples analyzed the fractional coverage was less than 22%, even though these samples fell within monolayer equivalence levels, which leads to the concept that organic matter is adsorbed in discrete patches and not as a monolayer. Visible and electron microscopy studies have also noted that organic matter appears to be present in discrete patches, rather than as a monolayer (Bishop et al., 1992; Ransom et al., 1997; Mayer, 1999).

This study looks at the monolayer equivalence levels (Mayer, 1994a; Mayer, 1994b), and fractional coverage (Mayer, 1999) for cores in the Makran area to determine if samples with monolayer equivalence levels that are indicative of a monolayer coating of organic matter do have a fractional coverage of approximately 100%.

Methods

Sample Collection

Samples were collected during the PAKOMIN, Pakistan-oxygen-minimum-zone, study of sediments on the Pakistan margin in 1990 on the German research vessel FS

Sonne. Surface sediments were collected with a 50 cm X 50 cm Kasten box-corer, and sub-sampled with 9 cm i.d. plastic tubes, which were then sectioned at 5 cm intervals for the first 5 cm and at 1cm intervals up to 10 cm and at 2 cm intervals below 10 cm. Samples were then frozen and stored at -20°C until being freeze dried. Samples from four coring sites were used for this study (Figure 1): 18 KG, 228 m water depth; 23 KG, 690 m water depth; 28 KG, 1017 m water depth; and 1 KG, 2678 m water depth.

Total Carbon And Total Nitrogen

Total carbon and total nitrogen were determined using flash-combustion gas chromatography on a Carlo-Erba NA 1500 CNS elemental analyzer. The operation of the analyzer and composition of the combustion column are similar to those described by Verardo (1990).

Inorganic Carbon

Inorganic carbon was determined using a UIC Coulometrics CO₂-coulometer. Samples were subjected to 10% hydrochloric acid, which reacts with the carbonate in the sample forming CO₂. The CO₂ is carried to the coulometer where it is quantified and integrated giving the inorganic carbon content.

Organic Carbon

The organic carbon content of each sample was determined using the difference between the total carbon, from flash combustion gas chromatography, and the inorganic carbon content, from coulometry.

Organic Matter Oxidation

Oxidation was done on all samples to remove the organic matter in order to measure the surface area of the naked mineral surfaces (Mayer, 1994a; Mayer, 1994b). Three methods of organic matter oxidation were tested to determine which was the most effective at removing organic matter from the sediment samples: (1) using 30% hydrogen peroxide; (2) using a mixture of sodium pyrophosphate (0.1 M) and 30% hydrogen peroxide (Sequi and Aringhieri, 1977); and (3) using sodium hypochlorite.

Each method was applied to a series of samples and then each sample, post-oxidation, was analysed for organic carbon content using the method described previously. Both the hydrogen peroxide method and the sodium hypochlorite method showed residual organic carbon concentration that was greater than could be explained by analytical error, additionally, the sodium hypochlorite method reacted with the manganese in some samples forming permanganate. The method using a combination of sodium pyrophosphate and hydrogen peroxide removed the organic matter more effectively than the other methods.

The samples were placed in a water bath at temperatures ranging from 70-80°C and were initially subjected to the 0.1 M sodium pyrophosphate and 30% hydrogen peroxide mixture (Sequi and Aringhieri, 1977), followed by aliquots of hydrogen

peroxides. This process was carried out for 48–96 hours, until CO₂ evolution ceased.

Samples were then rinsed three times to remove any residual salts and freeze dried.

Random samples were analyzed post oxidation for organic carbon content to determine if complete organic matter removal had occurred.

Carbon Stable Isotope Analysis

Carbon stable isotope ($\delta^{13}\text{C}$) analysis was carried out on all samples using a Carlo Erba Instruments Thermoquest NC 2500 elemental analyzer attached to a Finnigan, Delta Plus mass spectrometer. Samples were flash combusted and N₂ and CO₂ gases were separated in the elemental analyzer. The CO₂ gas enters the mass spectrometer where the amount of $\delta^{13}\text{C}$ is determined.

Surface Area

Surface area was determined using a Micromeritics® ASAP 2010 surface area analyzer by N₂ adsorption using multi-point BET (Brunauer-Emmett-Teller) method (Gregg and Sing, 1982). Surface area analysis was applied to samples both prior to and after organic matter oxidation. Samples were degassed at a constant temperature of 350°C for 3 – 4 hours. Following degassing samples were analysed using nitrogen as the sorbate at liquid nitrogen temperatures. The standard error of the method ranged from 2% to 4%.

Results

Organic Carbon & Nitrogen

Concentrations of organic carbon range from 5.0 to 24.8 mg C/g on a dry weight basis (Table 1), with the lowest organic carbon concentrations occurring at the shelf edge and increasing to a maximum along the continental slope (Figure 2 A, B, C, D). At the foot of the continental slope, at core site 1 KG, there is a notable decrease in organic carbon concentration when compared with core 28 KG. High organic carbon concentrations along the slope, at core site 23 KG, coincide with the oxygen minimum, which lies at depths between 200 and 800 m (Calvert et al., 1995; Cowie et al., 1999; Borole, 2002), whilst the highest concentration of organic carbon is in core 28 KG, which lies outside the oxygen minimum zone, but within the organic carbon concentration maximum zone. Cores from within the organic carbon concentration maximum zone (23 KG and 28 KG) have up to 5 times more organic carbon than the cores above or below the maximum (18 KG and 1 KG.)

All cores show some stratigraphic variability in organic carbon concentration (Figure 2 A, B, C, D), some cores (1 KG and 23 KG) more than others (28 KG.) In core 23 KG (Figure 2B), there is a decrease in organic carbon concentration between 5 cm and 10 cm within the sediment column. Organic carbon concentrations for this interval are similar to those found throughout core 18 KG (Figure 2A). In core 1 KG (Figure 2D), there is a increase in organic carbon concentration between 22 cm and 25 cm.

Organic nitrogen concentrations range from 0.04 to 0.34 % on a dry weight basis (Table 1). Depth profiles of organic nitrogen show similar variability as the depth profiles

of organic carbon (Figure 3), which further shows dilution and in some cases enrichment of organic matter as a result of sediment movement along the continental slope and shelf. Organic nitrogen profiles show low nitrogen concentrations on the shelf, with increasing nitrogen concentrations to a maximum at core site 28 KG, within the organic carbon concentration maximum zone.

The ratios of organic carbon to organic nitrogen in the Makran area range from 7.2 to 14.4 (Table 1), which is within the accepted range for marine derived organic matter. Cores outside the oxygen minimum zone and the organic carbon maximum zone have the highest organic carbon to organic nitrogen ratios; these cores also have the most stratigraphic variability with respect to organic carbon to organic nitrogen ratio. The average organic carbon to nitrogen ratio decreases with increasing core depth up to core 28 KG, at core site 1 KG the average organic carbon to nitrogen ratio increases.

Carbon Isotopes

Carbon isotopes measurements ($\delta^{13}\text{C}$) for the Makran area show very little variation both laterally and down core. Measurements generally vary from -19.4‰ to -21.7‰ (Table 1), which is typical of marine derived organic carbon (Pedersen et al., 1992).

Surface Area

The bulk sediment surface area for the Makran area ranges from 10.0 to 24.8 m^2/g (Table 1). Figure 4 shows that a trend of increasing average bulk sediment surface area

up to a water depth of 1017 m, core site 28 KG. In water depths greater than 1017 m, the average bulk sediment surface area decreases by approximately $5 \text{ m}^2/\text{g}$ at a water depth of 2678 m, core 1 KG. Cores 1 KG and 18 KG have similar average bulk sediment surface areas. Bulk sediment surface area values for each core site show variability on the order $10 \text{ m}^2/\text{g}$ (Figures 5A, B, C, and D). For many of the samples analyzed the surface area post organic matter oxidation is greater than pre-oxidation (Figure 6).

Surface Area and Organic Carbon

Samples from the Makran Area show very weak to no correlation between surface area and organic carbon (Figure 7). The correlation between organic matter and sediment surface area is greater at core sites 1 KG and 18 KG, than at core sites 23 KG and 28 KG (Figure 7). Cores 1 KG and 18 KG have bottom water oxygen concentrations of $105 \mu\text{M}$ and $23 \mu\text{M}$ respectively, which is greater than the bottom water oxygen concentrations for cores 23 KG and 28 KG (Cowie et al., 1999).

Organic Matter Coatings on Mineral Grains

The organic carbon to surface area ratios in the Makran area range from 0.28 to $1.50 \text{ mg OC m}^{-2}$ (Table 1), which covers the monolayer equivalence range 0.5 to 1.0 mg OC m^{-2} for marine sediments (Figure 8) (Mayer, 1994a; Mayer, 1994b). According to Mayer (1994), the organic carbon would be considered to be coating the sediment surfaces as a single molecule thick layer.

Cores 1 KG and 18 KG exhibit the lowest organic carbon to surface area ratios for the Makran area. Core 28 KG has the highest organic carbon to surface area ratios for the area. Low organic carbon to surface ratios in both cores 1 KG and 18 KG probably result from low organic carbon concentrations, whereas high organic carbon to surface area ratios in core 28 KG can be attributed to high organic carbon concentrations.

The majority of samples examined show evidence of a monolayer coating according to Mayer's (1994) definition of monolayer equivalence (Figure 8), however comparisons of enthalpies of adsorption of N_2 gas onto the mineral surfaces, both prior to and after the organic matter oxidation step, disagree with the notion that the organic matter is adsorbed onto the mineral surface in a monolayer. Sediments prior to the organic matter oxidation step show an inverse relationship between ΔH_{xs} values and the organic carbon-surface area ratio (Figure 9). When the organic matter is removed via oxidation, the correlation becomes weaker and the slope of the regression line becomes more positive (Figure 10). As ΔH_{xs} values are calculated based on the C constant, measured during multipoint-BET analysis of the samples, the increased correlation between ΔH_{xs} and organic carbon-surface area ratios for samples containing their original organic matter indicates that C constant measurements respond to natural organic matter concentrations and not to the mineral phases present in the sediment (Mayer, 1999). With organic matter removed the ΔH_{xs} values increased due to the greater enthalpies of adsorption onto mineral phases when compared to organic phases (Mayer, 1999).

Using the model for fractional coverage described by Mayer (1999), the ΔH_{xs} values calculated for both naked samples (samples having been oxidized to remove

organic matter) and coated samples (samples with their original natural organic matter) are compared to attain a fractional coverage of the organic matter over the mineral surfaces (Table 2). The result of such modeling for the Makran area shows that for the majority of the samples are not coated by a monolayer coating of organic, as defined by Mayer (1994ab). These samples have fractional coverage of the mineral surface that is less than 20% (Figure 11; Table 2). Only a few samples had fractional coverage values greater than 50% (Figure 11). Some samples with monolayer equivalence levels below that of a 'typical' marine shelf and slope environment show fractional coverage of the mineral surface that are greater than those in the 0.5 to 1.0 mg OC/m² range (Figure 11).

Discussion

Organic Matter Distribution

The Makran area receives a considerable amount of organic matter via marine primary production. In the eastern part of the Arabian Sea there are nearby rivers distributing terrestrial organic matter to the continental shelf and slope, however from both $\delta^{13}\text{C}$ and analysis and comparison of organic carbon to nitrogen ratios there is evidence that marine derived organic matter dominates the Makran area. Calvert et al. (1995) and Cowie et al. (1999) found that for the eastern Arabian Sea with increasing water depths organic carbon to nitrogen ratios decrease, indicating a distribution that is consistent with a contribution of a small amount of terrestrial organic matter to shallow-water area and an overwhelming dominance of planktonic marine organic matter to the deeper areas. Decreasing organic carbon to nitrogen ratios with increasing water depth

occurs in this study area (Figure 12), with the exception of the deepest core, 1 KG. The trend of decreasing organic carbon to nitrogen ratios in this study area may be related to a decrease in terrestrial organic matter content with increasing distance from the shore, however the lack of a major source of terrigenous organic matter, such as the Indus River, for the Makran area makes this theory unlikely. The decrease in organic carbon to organic nitrogen ratios across the continental shelf and slope can be attributed to the use of organic nitrogen by microbes in consuming organic matter in the shallower regions, whilst the organic matter in samples from the organic carbon concentration maximum are degraded to a lesser extent.

The distribution of the organic carbon along the continental shelf and slope is in keeping with studies of the northeastern Arabian Sea (Calvert et al., 1995; Cowie et al., 1999) and the western Arabian Sea (Pedersen et al., 1992). Organic carbon concentrations reach their maximum between water depths of 200 and 1600 m (Figure 13). Although there is a persistent oxygen minimum zone between 200 and 800 m water depth (Calvert et al., 1995), the highest organic carbon concentrations are found at depths greater than 800 m. High organic carbon concentrations outside the oxygen minimum zone are consistent over this region (Pedersen et al., 1992; Calvert et al., 1995; Cowie et al., 1999) and suggest that the role the oxygen minimum zone plays in enhancing organic carbon preservation is not a primary role.

Seismic activity of the Makran area, along with storm events, move sediment along the continental shelf and slope (Calvert et al., 1995; Staubwasser and Sirocko, 2001). The re-suspension and re-settling of sediment, and therefore movement of

sedimentary organic matter may explain the lack of homogeneity in organic matter distribution seen stratigraphically for all the cores. Sediment movement across the continental slope can carry organic-rich sediment from within the organic carbon concentration maximum to areas further seaward along the continental slope increasing the organic carbon concentrations in deeper cores. Conversely, sediment movement can also carry organic poor sediment from the shallower continental shelf seaward along the continental slope that, thus, can dilute the organic carbon concentration.

In core 23 KG, between core depths of 5 cm and 10 cm, the decrease in organic carbon concentrations can be attributed to dilution of the organic carbon content as a result of sediment re-distribution. Similarly, in core 1 KG, between core depths of 22 cm and 25 cm an increase in organic carbon concentration is likely the result of organic rich sediments being moved along the continental slope, possibly from within the oxygen maximum zone. Influxes of sediment to the cores sites from along the continental shelf and slope serve as plausible reasons as to why heterogeneity is observed through out the cores examined.

Surface Area

Bulk sediment surface areas for cores in the Makran area are typical of the continental shelf and slope sediment analyzed by Mayer (1994). The surface area increase between core 18 KG and 28 KG is the result of sediment particle size: coarser grained sediments settling closer to the coast while finer grained sediment is carried further out into the ocean. The anomalous decrease in bulk sediment surface areas for

core 1 KG, the furthest offshore core, is indicative of the heterogeneity as a result re-distribution of shelf and slope sediment, as discussed previously.

Similar to the results for organic carbon concentration, stratigraphically, the bulk sediment surface area in the Makran area shows variability on the order of $10 \text{ m}^2/\text{g}$. The observed variability further indicates that sediment movement along the continental shelf and slope is contributing to the heterogeneity.

Surface Area–Organic Carbon Relationship

There is a very poor correlation between surface area and organic carbon, which suggests that sediment surfaces are doing little to enhance organic matter preservation for this region. However, the poor correlation observed for this area may also be related to the sediment transport regime, which has been shown to move and re-distribute sediment, post deposition, along the continental shelf and slope, as observed in the heterogeneity of some cores. Movement of sediment may, therefore, be masking any enhancement of organic matter preservation via sediment surfaces. As seen in the organic carbon profiles, the organic carbon concentrations, stratigraphically, display heterogeneity. The heterogeneity has been proposed to be related to tectonic and storm events redistributing sediment along the continental shelf and slope. Similar re-distribution could result in sediment particles, which may have high surface area and large concentrations of organic carbon adsorbed on their surfaces, to be “plucked” from their original point of rest during deposition to a new depositional area. Depending on whether the new neighbouring sediment particles are equally, greater or less “coated” by adsorbed organic matter the

implied efficacy of these re-distributed sediment particle with respect organic matter adsorption and enhanced preservation of organic matter is either unchanged, improved, or diminished when looking at the bulk sediment surface area.

The poor correlations between surface area and organic carbon indicate that, for the Makran area, adsorption protection of organic matter plays, at best, a supplementary role in enhancing organic matter preservation. While the correlation between surface area and organic carbon is very poor, there is an increased correlation between organic carbon concentrations and sediment surface area in the cores with appreciable bottom water oxygen concentration, when compared with cores with low bottom water oxygen concentration in the same region. The increased correlation in the more oxic cores suggests that even though surface area does not appear to play a major role in enhancing organic matter preservation, surface area may be playing an additive role in enhancing organic matter preservation in the oxic regions of the Makran area. Typically, sedimentary organic matter exposed to oxic conditions is readily degraded by microbes, however the increased correlation outside the low oxygen regions in the Makran area, when compared with those samples from inside the low oxygen region, suggests that organic matter is being protected from complete degradation through adsorption onto sediment surfaces. Therefore, adsorption of organic matter onto sediment surfaces is more important in the oxic environments of the Makran area.

Other factors, such as organic matter supply play an equal or even more important role in aiding organic carbon preservation in the Arabian Sea (Pedersen et al., 1992; Calvert et al., 1995). With the large pulses of primary production that occur in the

Arabian Sea, the likelihood that an appreciable amount of organic matter survives settling through the water column to the sediment is increased.

Keil and Cowie (1999) argue that if organic matter supply were the dominating factor in the Arabian Sea, then the sediment underlying areas of high productivity would have high organic carbon concentrations. High organic carbon concentrations underlying highly productive regions are not seen in the data presented by Keil and Cowie (1999) nor are high organic carbon concentrations underlying highly productive areas found in the data presented in both this study and the studies by Calvert et al. (1995) and Cowie et al. (1999). Keil and Cowie (1999), therefore, suggest that a combination of mineral surface area and bottom water oxygen concentrations contribute to organic matter preservation. By comparing bottom-water oxygen with organic carbon to surface area ratios, Keil and Cowie (1999) conclude that the combination of organic matter protection onto mineral surfaces in conjunction with low bottom water oxygen concentrations enhances organic matter preservation (Figure 14a). For samples examined from the Makran area, by this study, (Figure 14b) there is no conclusive evidence to suggest that both bottom water oxygen concentrations and organic matter protection via adsorption onto mineral surfaces worked in conjunction to enhance preservation for the Makran Area. Furthermore, the data presented in this study suggests that the relationship between organic matter and surface area appears to be enhanced outside low oxygen zones.

Organic Matter Coatings

Mayer (1999) has questioned previous hypotheses that describe organic matter as being adsorbed onto mineral surfaces in monolayer coating based on a monolayer equivalence range. Recent studies, by Mayer (1999), Mayer and Xing (2001) and Mayer et al. (2002), have shown that even though samples may have organic carbon to surface area ratios that are within the monolayer equivalence range, the same samples have fractional coverage values that show the organic matter is covering less than 22% of the mineral surfaces.

The Makran area of the Arabian Sea shows similar results to those found by Mayer (1999), Mayer and Xing (2001) and Mayer et al. (2002), the majority of samples analyzed that have organic carbon to surface area ratios within the monolayer equivalence range, as defined by Mayer (1994a; Mayer, 1994b), have less than 20% fractional coverage (Figure 11). If the organic matter is coating the surfaces of the mineral grains as a monolayer coating, then the fractional coverage should be approximately 100%, which is not the case for the Makran area. Therefore, the organic coatings on mineral grain in the Makran area are not monolayer in nature. The organic matter is adsorbed in discrete patches across the mineral surface, adsorbing onto high enthalpy adsorption sites. Increases in surface area as a result of organic matter removal from sediment surfaces indicate that organic matter adsorption occurs on topographic lows on the sediment surfaces (Weiler and Mills, 1965; Mayer, 1994a; Mayer, 1994b), the topographic lows might be indicative of high enthalpy adsorption sites.

Conclusion

The Makran area of the Arabian Sea shows no significant relationship between organic carbon concentrations and bulk sediment surface area, which suggests that surface area has little to no effect on enhancing organic carbon preservation.

The stratigraphic variability of organic carbon concentrations, organic nitrogen concentrations, and $\delta^{13}\text{C}$ are indicative of sediment re-distribution as a result of seismic activity and storm events transporting sediment across the continental shelf and slope. The active movement of sediment across the shelf and slope in this region could result in the lack of correlation between organic carbon concentration and bulk sediment surface area.

Organic matter coatings on mineral grains show monolayer equivalence levels for the Makran area, however when fractional coverage is calculated the data showed that less than 20% of the surfaces were coated by organic matter. The organic matter is either adsorbed in discrete patches on the mineral surfaces; or the organic matter is adsorbed as a single molecule thick monolayer on some mineral grains while other grains are either coated by discrete patches of organic matter or not coated at all. In light of recent studies (Mayer, 1999; Bock and Mayer, 2000; Mayer and Xing, 2001) it seems more plausible that the former is true. Further analysis via size fractionating samples may determine whether some of the mineral size fractions have a propensity to be coated via a monolayer whilst others are either not coated at all or coated in discrete patches, or whether all mineral grains are similarly coated in discrete patches.

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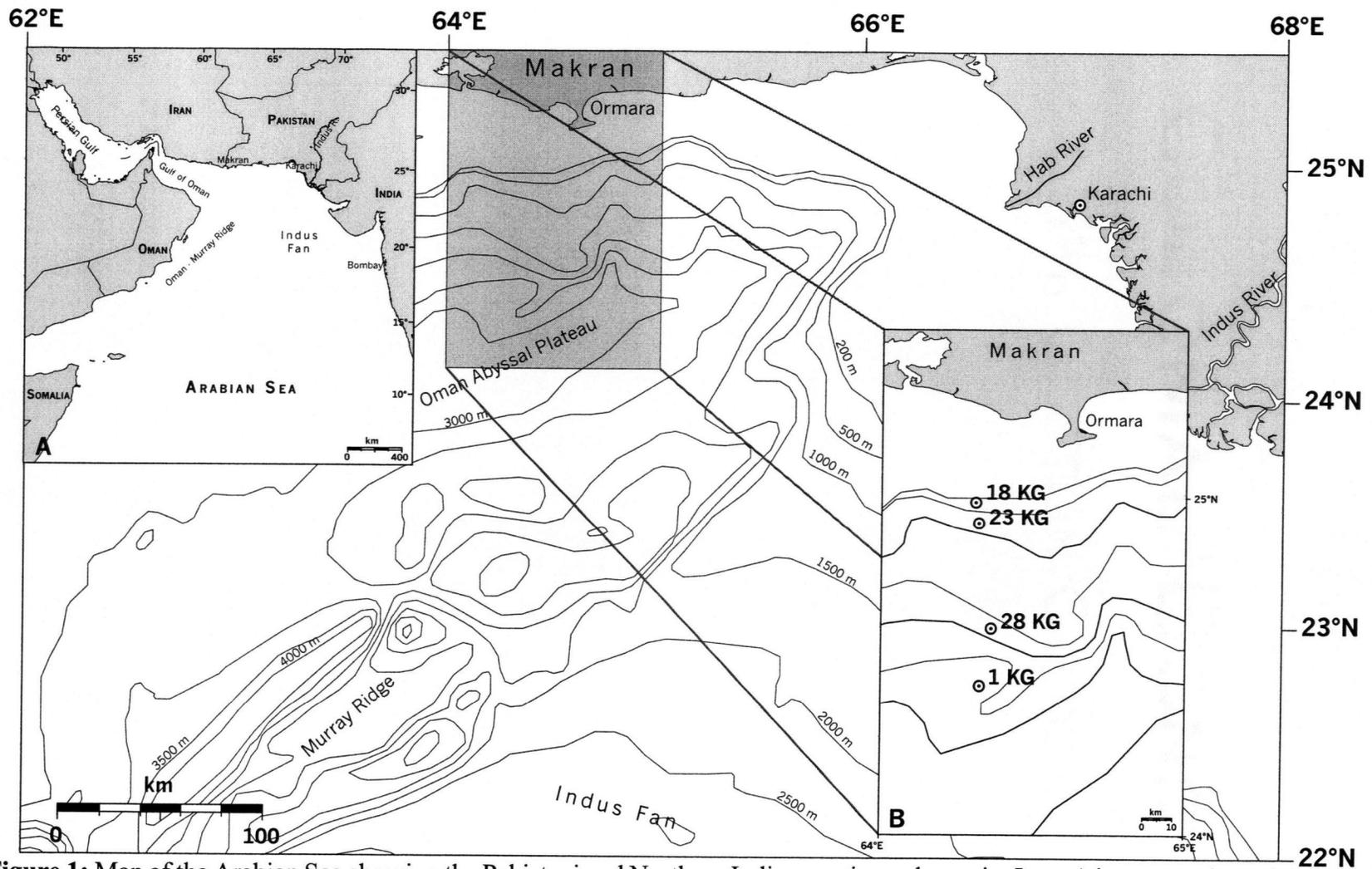


Figure 1: Map of the Arabian Sea showing the Pakistani and Northern Indian continental margin. Inset A is an overview of the entire Arabian Sea region. Inset B shows the Makran area and sample sites (18 KG, 23 KG, 28 KG and 1 KG) in greater detail.

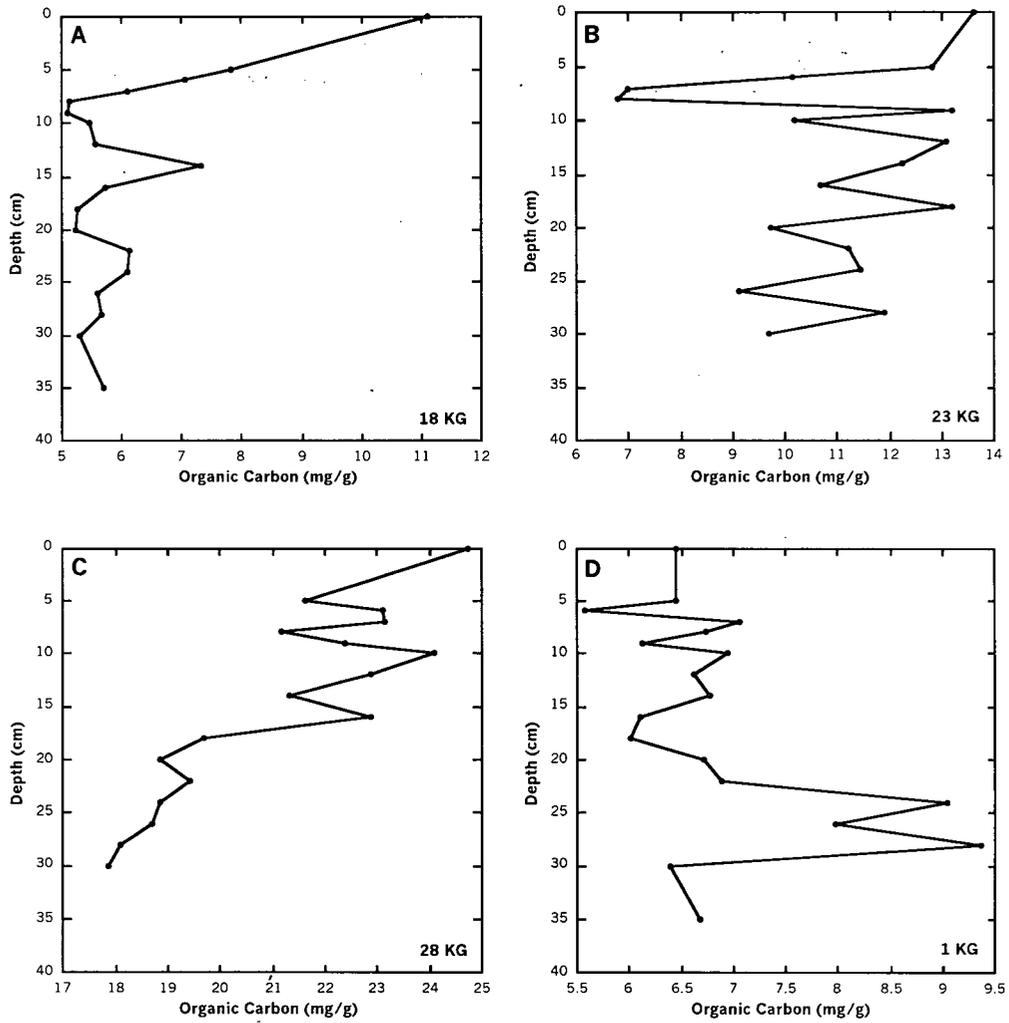


Figure 2: Organic carbon depth profiles for core A) 18 KG, at a water depth of 269 m; B) 23 KG, at a water depth of 690 m; C) 28 KG, at a water depth of 1017 m; and D) 1 KG, at a water depth of 2700 m.

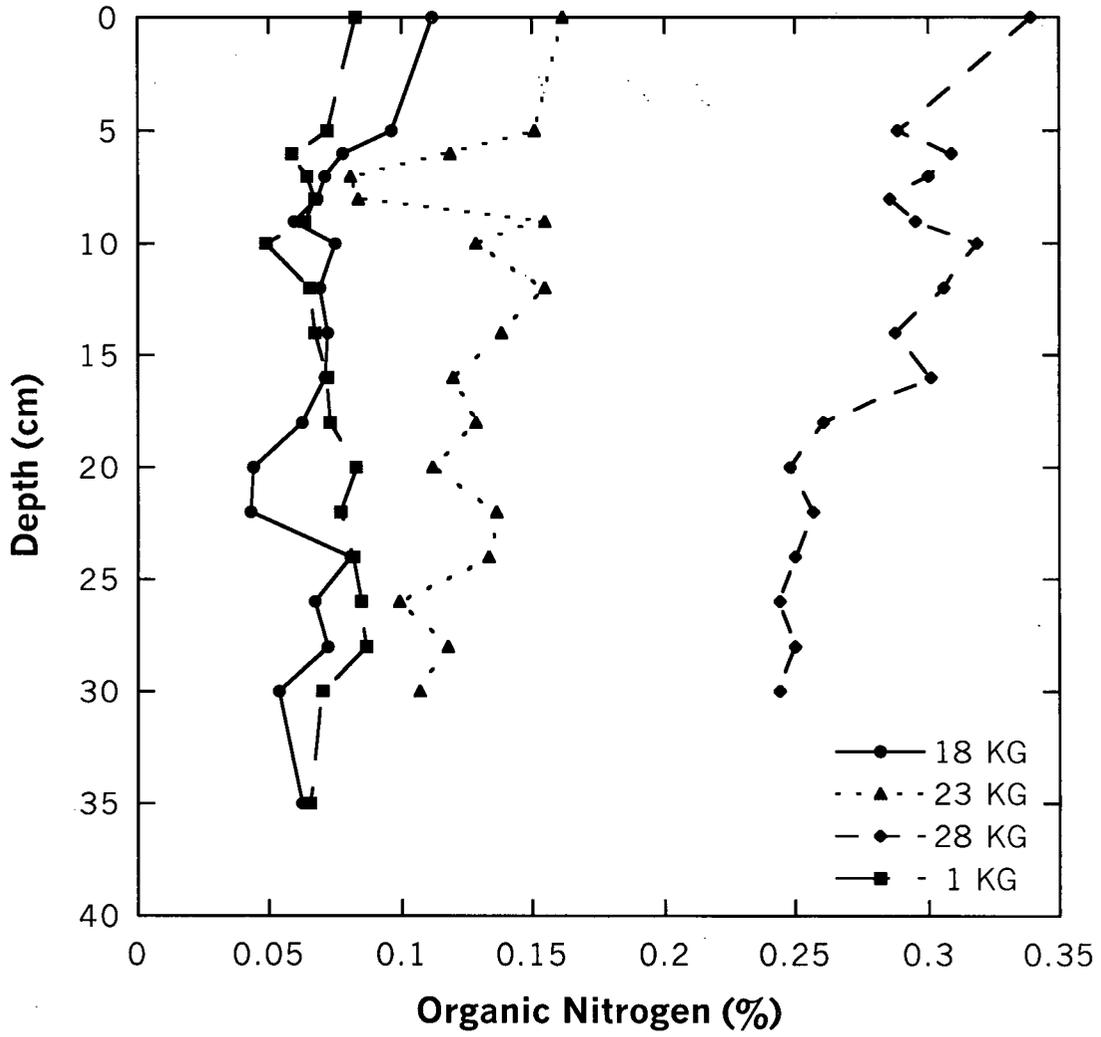


Figure 3: Organic nitrogen depth profiles for the Makran area.

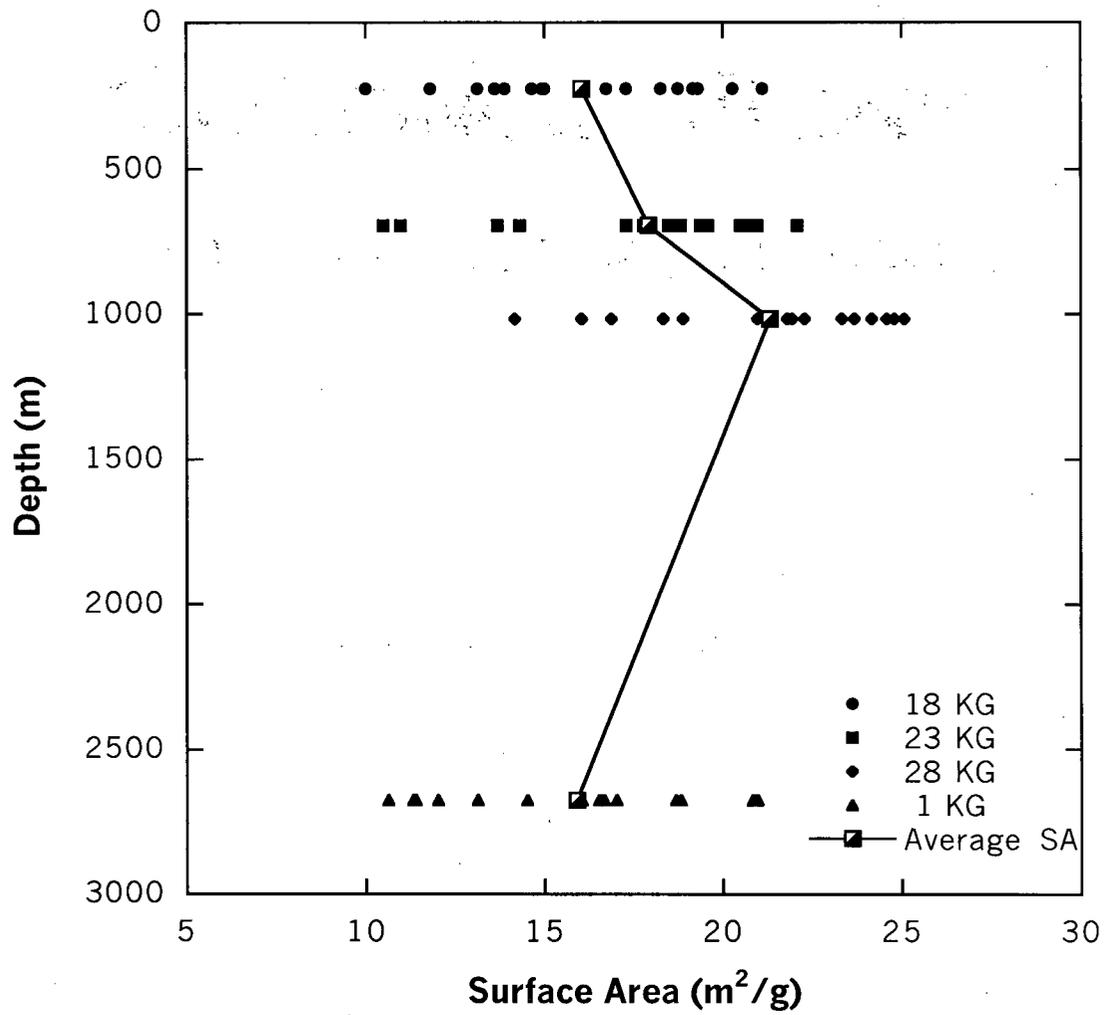


Figure 4: Surface area plotted against depth below the sea surface at each core site. The line drawn through the data points at each core depth is the average surface area determined for that core site.

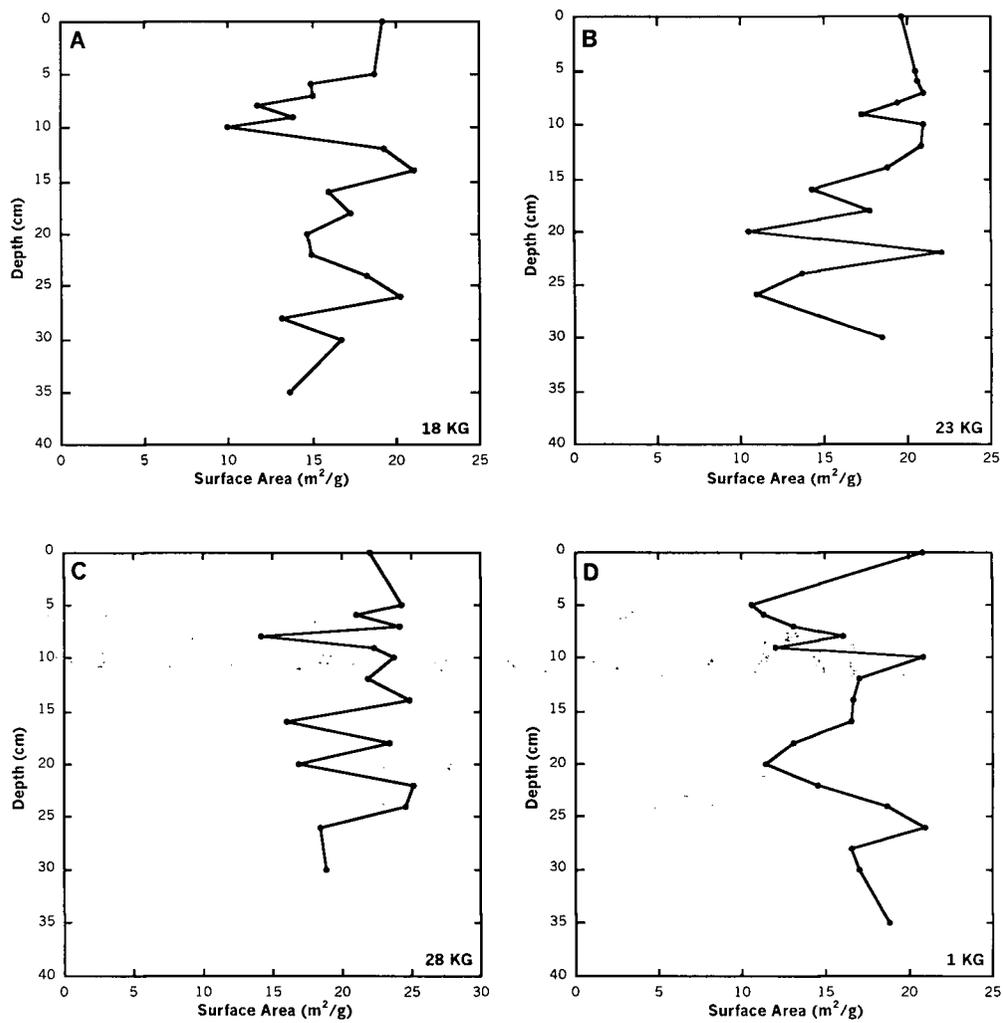


Figure 5: Bulk sediment surface area depth profiles for core A) 18 KG, at a water depth of 269 m; B) 23 KG, at a water depth of 690 m; C) 28 KG, at a water depth of 1017 m; and D) 1 KG, at a water depth of 2700 m. Surface area measurements shown are of oxidized sample, without organic matter.

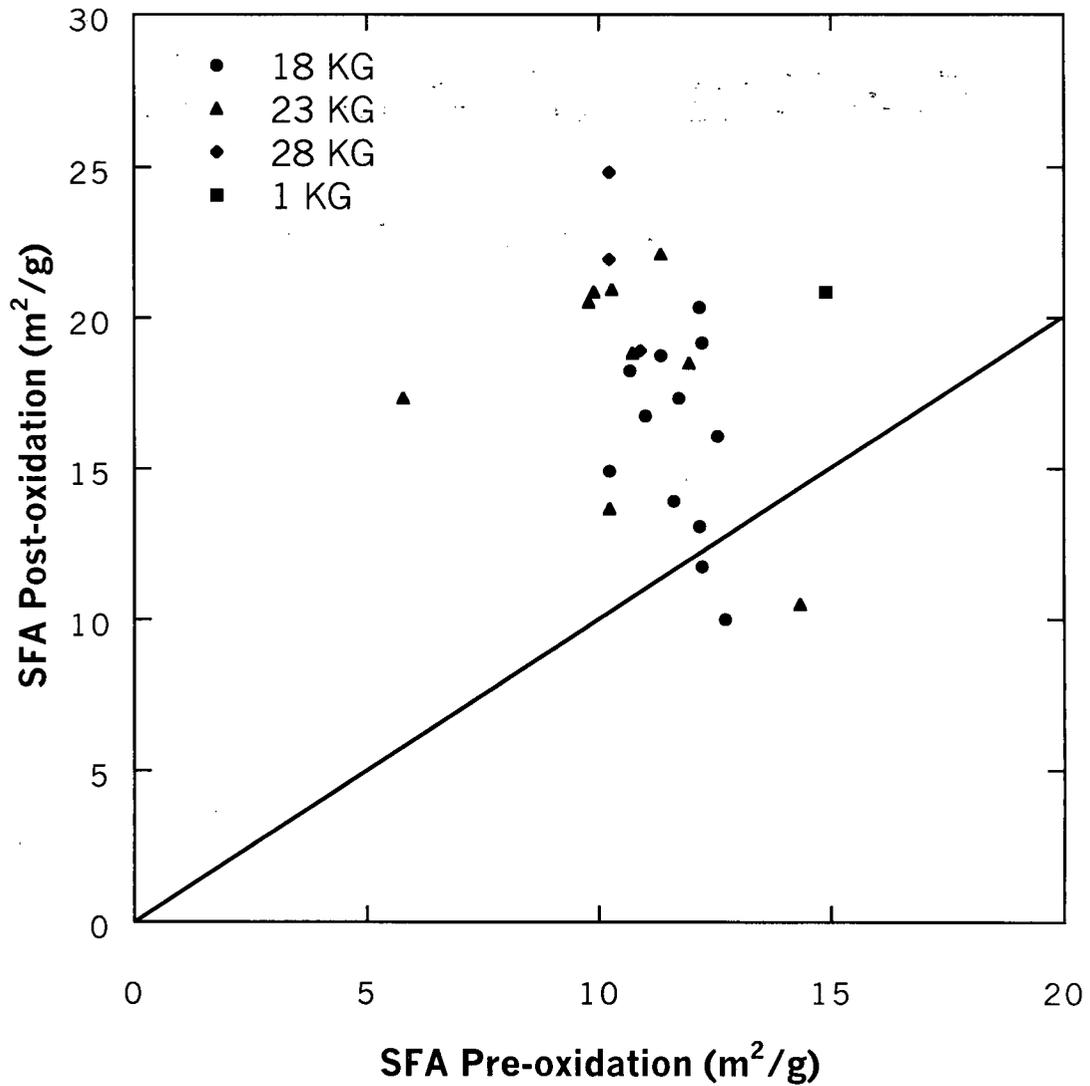


Figure 6: Scatter plot of bulk sediment surface area (SFA) prior to organic matter being oxidized versus bulk sediment SFA after the organic matter has been oxidized. Points that lie on the 1:1 line running through the origin indicate no change in SFA as a result of organic matter removal, points that lie above the 1:1 line indicate as a result of organic matter oxidation the bulk sediment SFA has increased, whilst points that lie below the 1:1 line indicate that there is a loss of bulk SFA after organic matter oxidation.

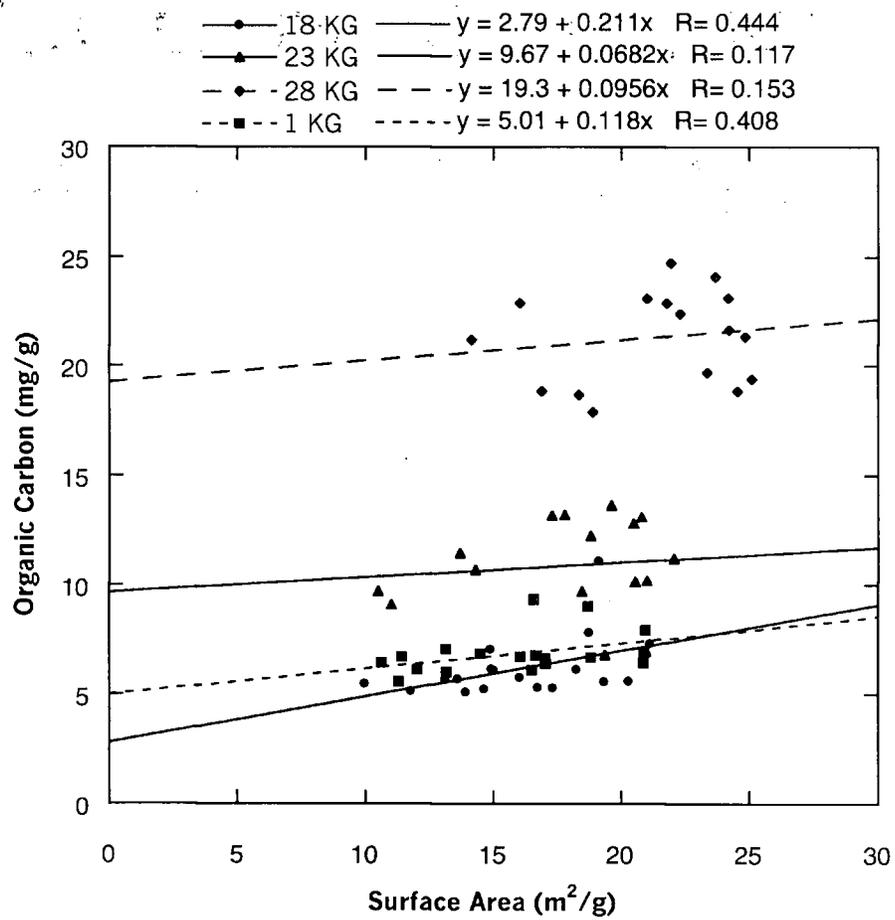


Figure 7: Scatter plot of bulk sediment surface area versus organic carbon for all core sites. Note: Cores outside the organic carbon concentration maximum zone show a greater correlation between bulk sediment surface area and organic carbon than those cores inside the organic carbon concentration maximum.

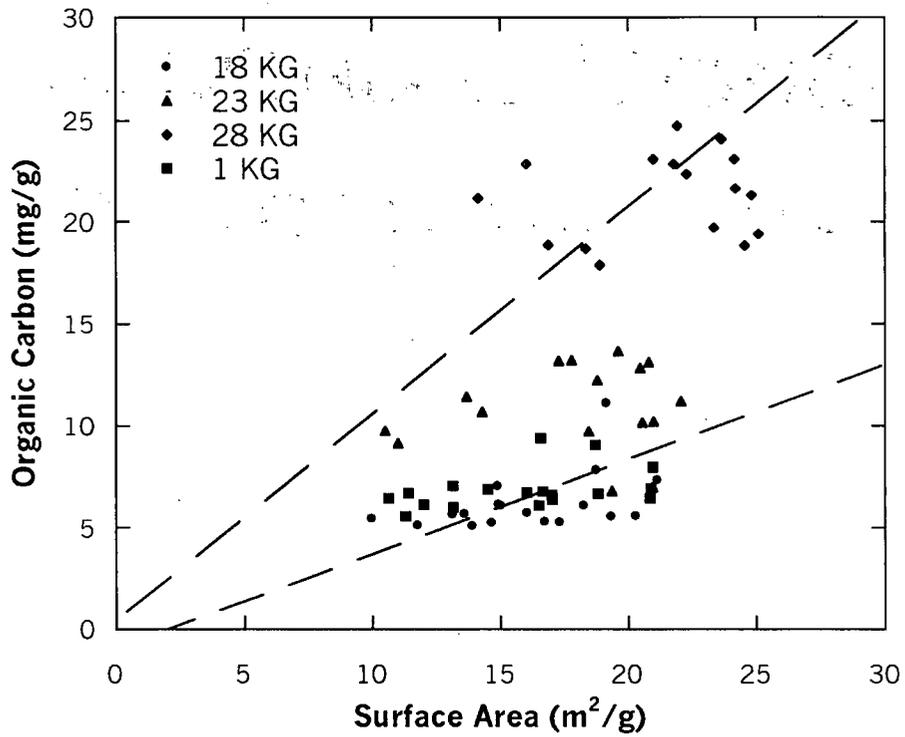


Figure 8: Scatter plot of bulk sediment surface area versus organic carbon for all core sites in the Makran area. The dashed lines that intersect the axis are the upper, 1.0 mg OC/m², and lower, 0.5 mg OC/m², limits of the monolayer equivalence layer level for marine sediments (Mayer, 1994a; Mayer, 1994b).

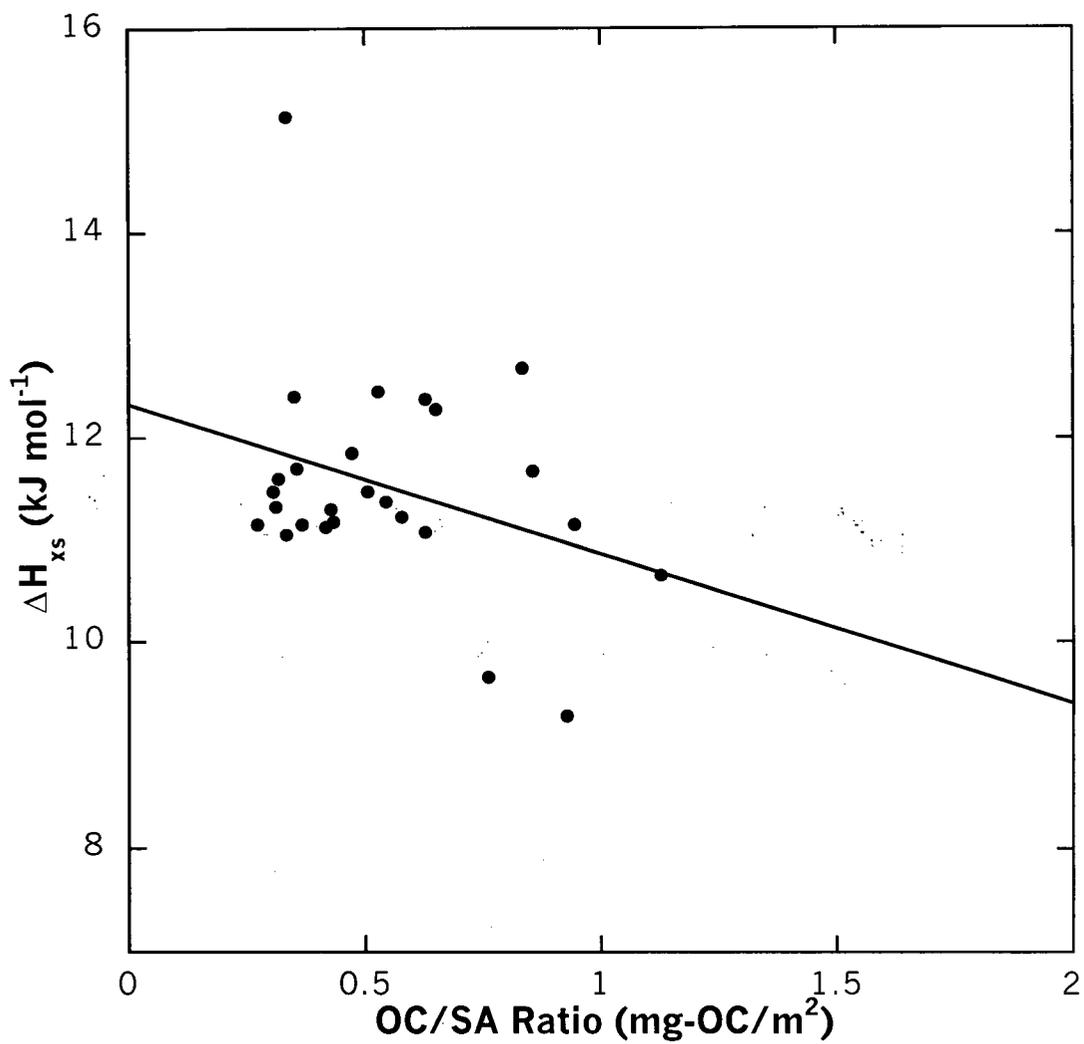


Figure 9: Enthalpy of adsorption (ΔH_{xs}) of N_2 gas onto the sediment samples prior to organic matter oxidation versus organic carbon to bulk sediment surface area ratios.

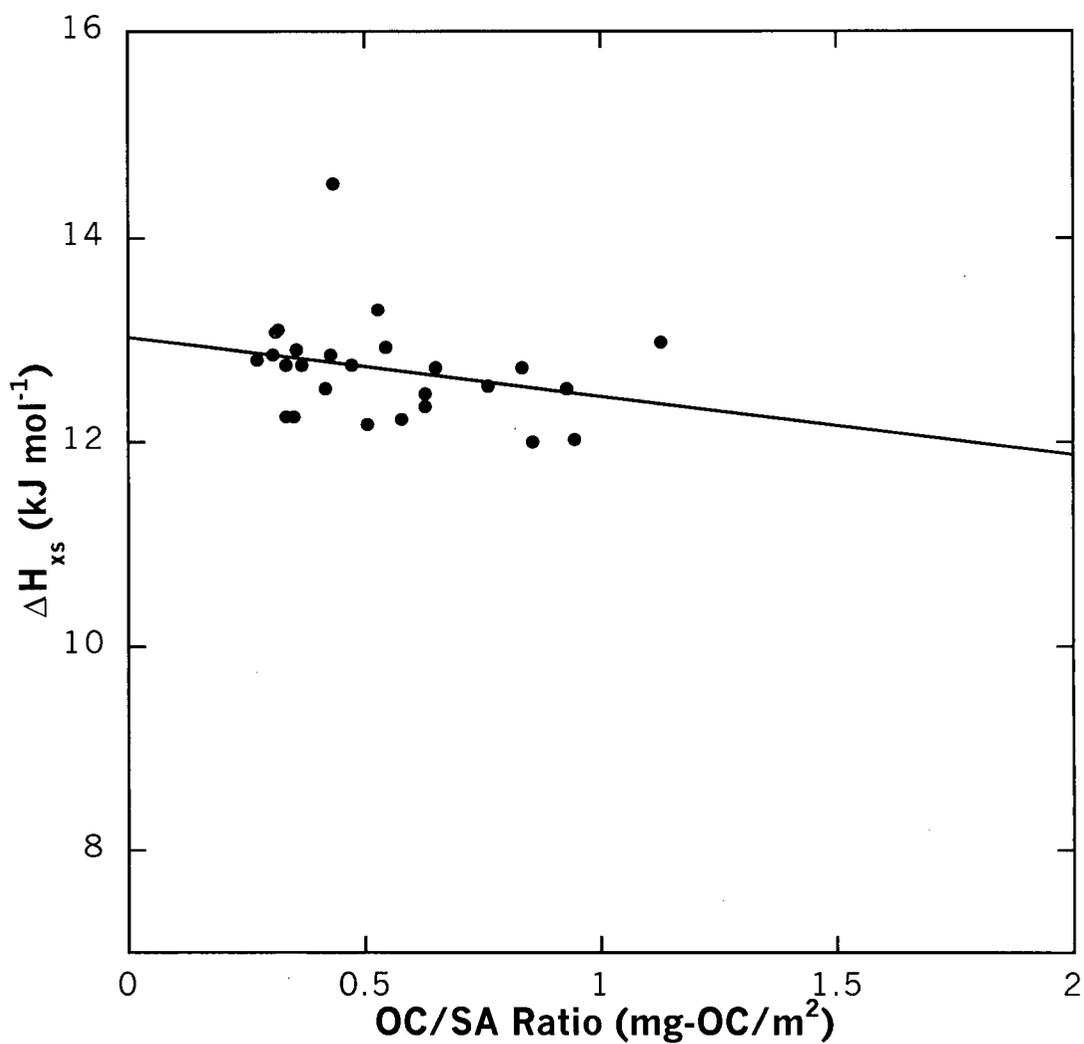


Figure 10: Enthalpy of adsorption (ΔH_{xs}) of N_2 gas onto the sediment samples after organic matter oxidation versus organic carbon to bulk sediment surface area ratios.

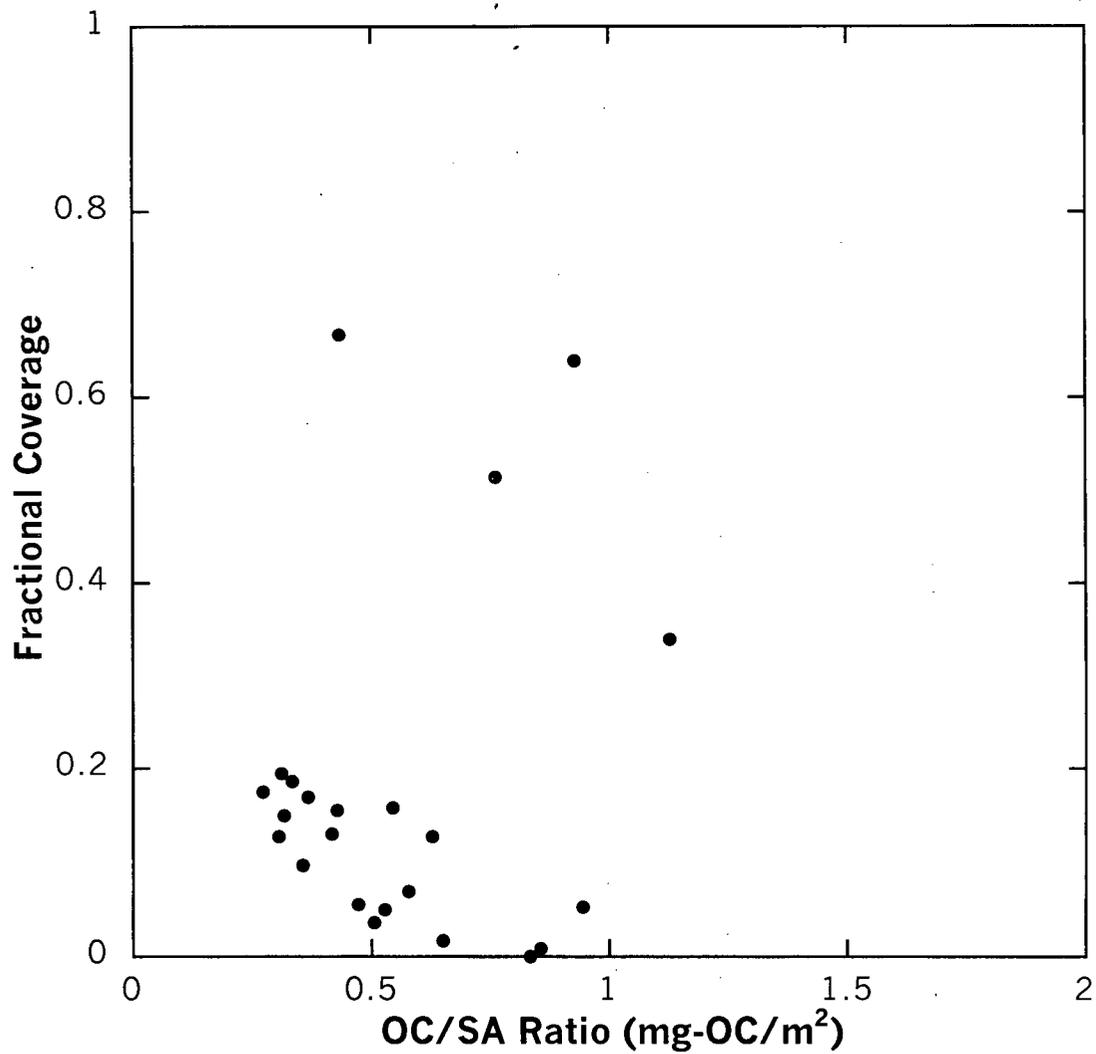


Figure 11: Scatter plot comparing the organic carbon to bulk sediment surface area ratios and fractional coverage of the sediment particles. Fraction coverage values have been determined using Mayer (1999).

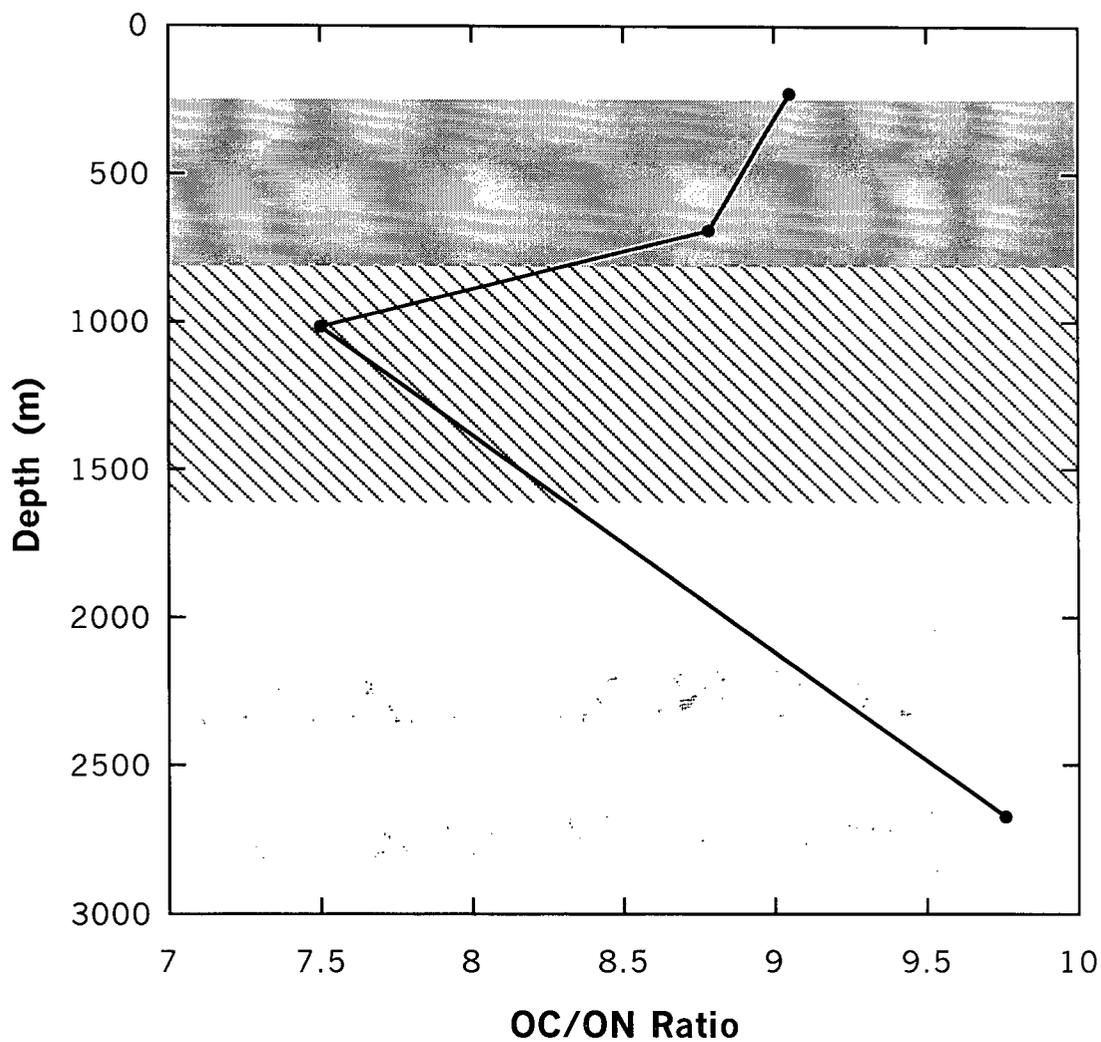


Figure 12: Plot comparing the average organic carbon to organic nitrogen ratios and the water depths of the cores. Average organic carbon to organic nitrogen ratios are calculated from the entire core at a given water depth. The shaded region denotes the oxygen minimum zone, whilst the hatched region combined with the shaded region denotes the organic carbon concentration maximum zone (Calvert et al., 1995).

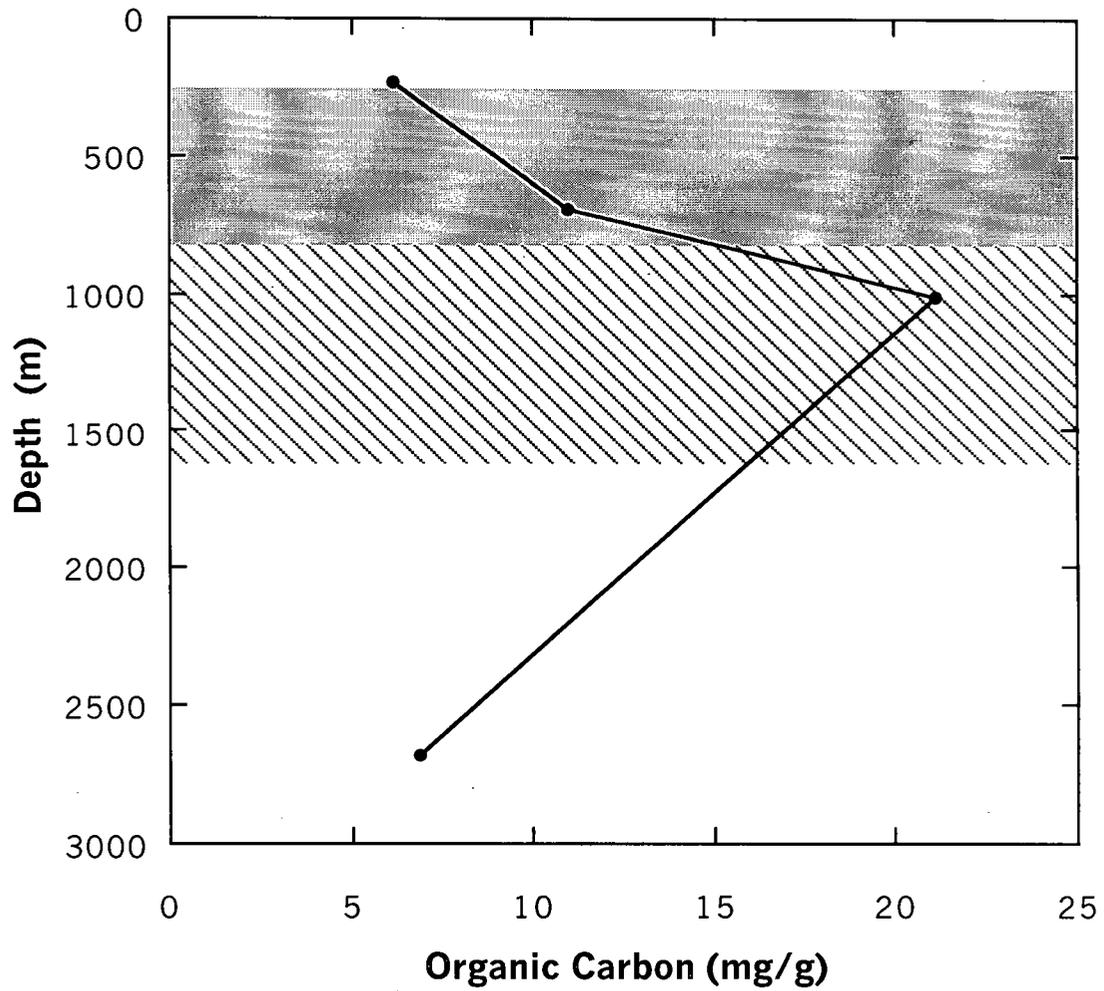


Figure 13: Plot comparing the average organic carbon concentration and the water depth of the cores studied. The average organic carbon concentrations are calculated using the entire core at a given water depth. The shaded region denotes the oxygen minimum zone, whilst the hatched region denotes the organic carbon concentration maximum zone.

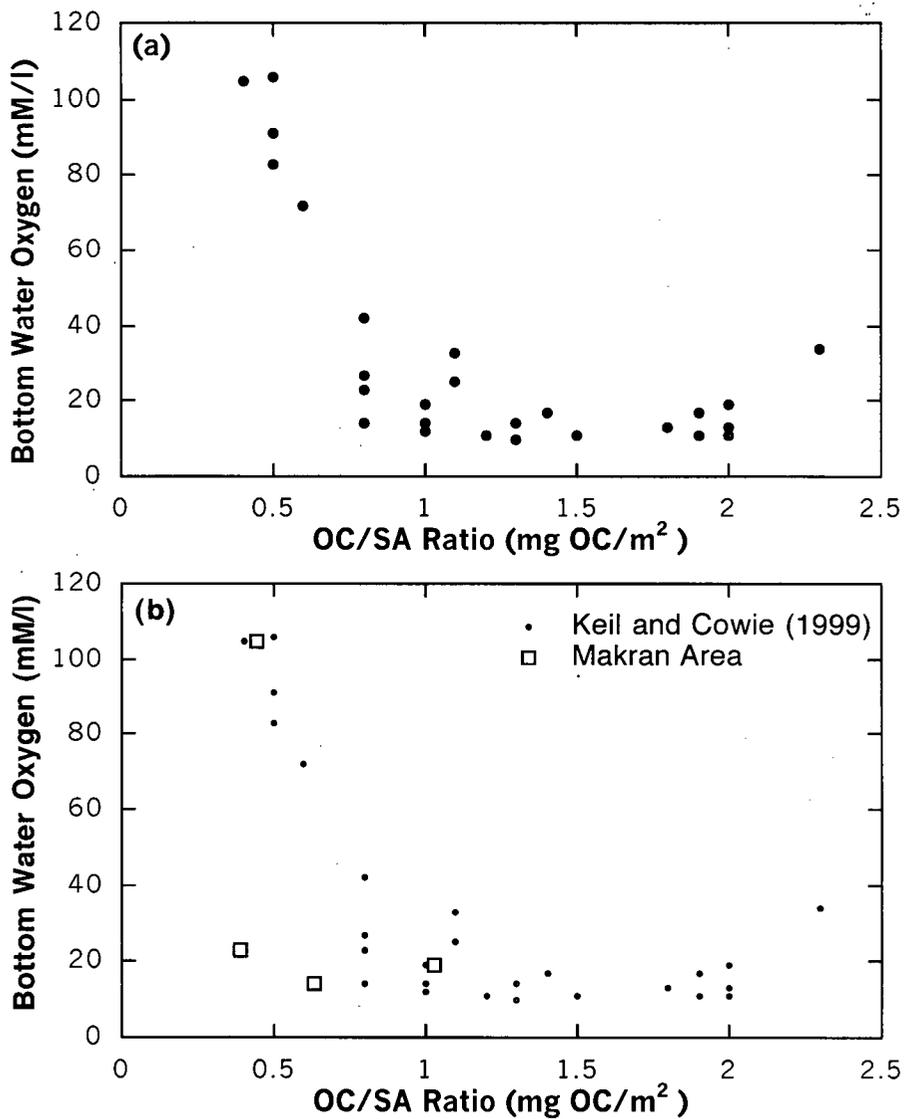


Figure 14: Scatter plots comparing the organic carbon to surface area ratios of samples from the Arabian Sea with bottom water oxygen concentrations. (a) Data from Keil and Cowie (1999) for the northern Arabian Sea. (b) Data from Keil and Cowie (1999), filled circles, compared with data from this study, open squares.

Table 1: Surface area pre-organic matter oxidation, SA_{PRE}, surface area post-organic matter oxidation, SA_{POST}, total carbon, TC, inorganic carbon, IOC, organic carbon, OC, total nitrogen, TN, organic nitrogen, ON, organic carbon to organic nitrogen ratio, OC/ON, organic carbon to surface area ratio, OC/SA, and $\delta^{13}\text{C}$ data for the cores from the Makran area.

Core: 18 KG

Depth (cm)	SA _{PRE} (m ² /g)	SA _{POST} (m ² /g)	TC (%)	IOC (%)	OC (%)	OC (mg/g)	TN (%)	ON (%)	OC/ON	OC/SA (mg/m ²)	$\delta^{13}\text{C}$ (‰)
0	12.25	19.15	2.62	1.52	1.11	11.09	0.176	0.131	8.50	0.58	-19.30
5	11.33	18.76	2.18	1.40	0.78	7.82	0.160	0.114	6.84	0.42	-19.51
6	10.22	14.90	2.14	1.44	0.70	7.05	0.143	0.097	7.26	0.47	-19.69
7	.	15.02	2.05	1.44	0.61	6.10	0.135	0.089	6.82	0.41	-19.85
8	12.21	11.78	2.03	1.52	0.51	5.11	0.133	0.087	5.86	0.43	-19.91
9	11.63	13.92	2.04	1.53	0.51	5.09	0.124	0.078	6.50	0.37	-20.04
10	12.70	9.98	2.02	1.48	0.54	5.45	0.139	0.094	5.83	0.55	-19.98
12	.	19.34	2.08	1.53	0.55	5.54	0.134	0.088	6.31	0.29	-19.85
14	.	21.14	1.94	1.21	0.73	7.32	0.136	0.091	8.07	0.35	-19.74
16	12.56	16.05	1.99	1.42	0.57	5.74	0.136	0.090	6.37	0.36	-19.81
18	11.73	17.33	2.03	1.50	0.53	5.27	0.127	0.081	6.52	0.30	-19.79
20	.	14.66	2.12	1.60	0.52	5.23	0.108	0.063	8.34	0.36	-19.74
22	.	14.93	2.08	1.47	0.61	6.13	0.107	0.061	9.98	0.41	-19.71
24	10.67	18.27	2.00	1.39	0.61	6.10	0.145	0.099	6.14	0.33	-19.75
26	12.14	20.30	2.08	1.52	0.56	5.58	0.132	0.086	6.48	0.27	-19.71
28	12.15	13.13	2.08	1.52	0.56	5.64	0.136	0.091	6.23	0.43	-19.61
30	11.00	16.74	2.04	1.51	0.53	5.29	0.118	0.072	7.30	0.32	-19.73
35	.	13.61	2.08	1.52	0.57	5.68	0.127	0.081	7.01	0.42	-19.66
Average:	11.72	16.06	2.09	1.47	0.62	6.18	0.134	0.089	7.02	0.39	-19.74

Table 1: (continued)

Core: 23 KG											
Depth (cm)	SA _{PRE} (m ² /g)	SA _{POST} (m ² /g)	TC (%)	IOC (%)	OC (%)	OC (mg/g)	TN (%)	ON (%)	OC/ON	OC/SA (mg/m ²)	δ ¹³ C (‰)
0	.	20.14	2.67	1.31	1.36	13.63	0.225	0.170	8.01	0.68	-20.22
5	9.75	20.48	2.66	1.38	1.28	12.83	0.214	0.160	8.03	0.63	-20.22
6	.	20.56	2.37	1.35	1.02	10.15	0.182	0.128	7.94	0.49	-20.23
7	10.25	20.96	1.92	1.22	0.70	6.98	0.144	0.090	7.77	0.33	-20.33
8	11.25	19.37	2.00	1.32	0.68	6.81	0.148	0.094	7.27	0.35	-20.05
9	5.75	17.30	2.72	1.40	1.32	13.19	0.218	0.164	8.05	0.76	-19.95
10	.	21.00	2.37	1.35	1.02	10.21	0.192	0.137	7.45	0.49	-19.99
12	9.89	20.80	2.75	1.44	1.31	13.10	0.218	0.164	7.99	0.63	-19.95
14	10.73	18.80	2.64	1.42	1.22	12.24	0.201	0.147	8.34	0.65	-20.07
16	.	14.29	2.45	1.38	1.07	10.69	0.184	0.130	8.24	0.75	-20.19
18	.	17.79	2.61	1.29	1.32	13.20	0.192	0.138	9.60	0.74	-20.37
20	14.35	10.49	2.31	1.34	0.97	9.72	0.176	0.121	8.02	0.93	-20.15
22	11.32	22.07	2.50	1.38	1.12	11.20	0.199	0.145	7.73	0.51	-20.11
24	10.22	13.69	2.56	1.42	1.14	11.44	0.197	0.143	8.02	0.84	-20.17
26	.	11.01	2.29	1.38	0.91	9.12	0.163	0.108	8.42	0.83	-19.95
28	.	.	2.56	1.37	1.19	11.91	0.181	0.127	9.40	.	-20.39
30	11.96	18.47	2.36	1.39	0.97	9.72	0.171	0.116	8.36	0.53	-19.85
Average:	10.55	17.95	2.46	1.36	1.09	10.95	0.189	0.134	8.15	0.63	-20.13

Table 1: (continued)

Core: 28 KG												
Depth (cm)	SA _{PRE} (m ² /g)	SA _{POST} (m ² /g)	TC (%)	IOC (%)	OC (%)	OC (mg/g)	TN (%)	ON (%)	OC/ON	OC/SA (mg/m ²)	δ ¹³ C (‰)	
0	10.23	21.94	4.15	1.68	2.47	24.74	0.342	0.341	7.26	1.13	-20.05	
5	-	24.20	3.36	1.20	2.16	21.64	0.291	0.290	7.46	0.89	-20.06	
6	-	21.00	3.55	1.24	2.31	23.12	0.312	0.310	7.45	1.10	-19.97	
7	-	24.16	3.53	1.22	2.31	23.13	0.302	0.301	7.68	0.96	-19.99	
8	-	14.14	3.27	1.15	2.12	21.18	0.288	0.287	7.38	1.50	-20.06	
9	-	22.30	3.34	1.10	2.24	22.39	0.298	0.297	7.54	1.00	-20.12	
10	-	23.66	3.67	1.26	2.41	24.10	0.322	0.320	7.53	1.02	-19.91	
12	-	21.78	3.59	1.30	2.29	22.89	0.308	0.307	7.46	1.05	-19.97	
14	10.21	24.83	3.55	1.42	2.13	21.32	0.290	0.289	7.37	0.86	-20.11	
16	-	16.02	3.78	1.49	2.29	22.89	0.304	0.302	7.57	1.43	-19.93	
18	-	23.36	3.35	1.38	1.97	19.70	0.263	0.262	7.52	0.84	-19.95	
20	-	16.89	3.34	1.45	1.89	18.86	0.251	0.250	7.56	1.12	-20.03	
22	-	25.09	3.32	1.38	1.94	19.41	0.259	0.258	7.52	0.77	-19.87	
24	-	24.55	3.31	1.43	1.88	18.84	0.253	0.251	7.49	0.77	-19.87	
26	-	18.35	3.38	1.51	1.87	18.69	0.247	0.245	7.61	1.02	-20.14	
28	-	-	3.25	1.44	1.81	18.08	0.252	0.251	7.21	-	-19.95	
30	10.91	18.90	3.36	1.57	1.79	17.88	0.246	0.245	7.31	0.95	-19.91	
Average:	10.45	21.32	3.48	1.37	2.11	21.11	0.284	0.283	7.47	1.03	-19.99	

Table 1: (continued)

Core: 1 KG

Depth (cm)	SA _{PRE} (m ² /g)	SA _{POST} (m ² /g)	TC (%)	IOC (%)	OC (%)	OC (mg/g)	TN (%)	ON (%)	OC/ON	OC/SA (mg/m ²)	δ ¹³ C (‰)
0	14.89	20.85	2.07	1.43	0.65	6.45	0.140	0.144	4.48	0.31	-21.36
5	.	10.62	2.10	1.46	0.64	6.45	0.130	0.134	4.82	0.61	-20.07
6	.	11.29	2.09	1.53	0.56	5.58	0.115	0.119	4.68	0.49	-20.07
7	.	13.13	2.23	1.53	0.71	7.07	0.122	0.125	5.64	0.54	-19.88
8	.	16.04	2.19	1.52	0.67	6.74	0.125	0.129	5.23	0.42	-19.99
9	.	12.01	2.23	1.62	0.61	6.14	0.121	0.125	4.92	0.51	-20.01
10	.	20.89	2.26	1.57	0.69	6.94	0.106	0.110	6.31	0.33	-19.85
12	.	17.01	2.19	1.53	0.66	6.63	0.123	0.127	5.23	0.39	-19.90
14	.	16.65	2.03	1.35	0.68	6.78	0.125	0.129	5.26	0.41	-19.87
16	.	16.50	2.02	1.41	0.61	6.12	0.130	0.134	4.57	0.37	-20.17
18	.	13.15	2.08	1.48	0.60	6.01	0.131	0.135	4.45	0.46	-20.04
20	.	11.41	2.10	1.43	0.67	6.72	0.141	0.144	4.65	0.59	-19.92
22	.	14.50	2.16	1.47	0.69	6.88	0.135	0.139	4.96	0.47	-19.75
24	.	18.71	2.21	1.31	0.90	9.05	0.140	0.144	6.29	0.48	-19.74
26	.	20.95	2.22	1.42	0.80	7.97	0.142	0.146	5.45	0.38	-19.76
28	.	16.58	2.27	1.33	0.94	9.37	0.144	0.148	6.33	0.57	-19.62
30	.	17.05	2.07	1.43	0.64	6.40	0.128	0.132	4.85	0.38	-19.75
35	.	18.81	2.05	1.38	0.67	6.69	0.123	0.127	5.27	0.36	-19.64
Average:	14.89	15.90	2.14	1.45	0.69	6.89	0.129	0.133	5.19	0.45	-19.97

Table 2: Surface area pre-organic matter oxidation, SA_{PRE} , surface area post-organic matter oxidation, SA_{POST} , organic carbon, OC, enthalpy of adsorption for samples with organic matter removed, ΔH_{xs} Naked, enthalpy of adsorption for samples with organic matter coatings, ΔH_{xs} Coated, fractional coverage calculated using Mayer (1999), FC^* , and fractional coverage using Mayer and Xing (2001), FC^{**} .

Core	Depth (cm)	SA_{PRE} (m^2/g)	SA_{POST} (m^2/g)	OC (mg/g)	ΔH_{xs} Naked	ΔH_{xs} Coated	FC^*	FC^{**}
1 KG	0.0	14.89	20.85	6.45	13.07	11.34	0.20	0.29
18 KG	0.0	12.25	19.15	11.09	12.23	11.23	0.07	0.36
18 KG	5.0	11.33	18.76	7.82	12.52	11.12	0.13	0.40
18 KG	6.0	10.22	14.90	7.05	12.74	11.85	0.06	0.31
18 KG	8.0	12.21	11.78	5.11	14.52	11.18	0.67	-0.04
18 KG	9.0	11.63	13.92	5.09	12.76	11.16	0.17	0.16
18 KG	10.0	12.70	9.98	5.45	12.92	11.37	0.16	-0.27
18 KG	16.0	12.56	16.05	5.74	12.89	11.70	0.10	0.22
18 KG	18.0	11.73	17.33	5.27	12.86	11.48	0.13	0.32
18 KG	24.0	10.67	18.27	6.10	12.75	11.06	0.19	0.42
18 KG	26.0	12.14	20.30	5.58	12.79	11.16	0.17	0.40
18 KG	28.0	12.15	13.13	5.64	12.84	11.31	0.16	0.07
18 KG	30.0	11.00	16.74	5.29	13.10	11.59	0.15	0.34
23 KG	5.0	9.75	20.48	12.83	12.47	11.09	0.13	0.52
23 KG	7.0	10.25	20.96	6.98	12.24	15.12	.	0.51
23 KG	8.0	11.25	19.37	6.81	12.25	12.41	.	0.42
23 KG	9.0	5.75	17.30	13.19	12.54	9.64	0.51	0.67
23 KG	12.0	9.89	20.80	13.10	12.34	12.39	.	0.52
23 KG	14.0	10.73	18.80	12.24	12.73	12.27	0.02	0.43
23 KG	20.0	14.35	10.49	9.72	12.52	9.26	0.64	-0.37
23 KG	22.0	11.32	22.07	11.20	12.18	11.47	0.04	0.49
23 KG	24.0	10.22	13.69	11.44	12.74	12.67	0.00	0.25
23 KG	30.0	11.96	18.47	9.72	13.30	12.46	0.05	0.35
28 KG	0.0	10.23	21.94	24.74	12.98	10.65	0.34	0.53
28 KG	14.0	10.21	24.83	21.32	11.99	11.67	0.01	0.59
28 KG	30.0	10.91	18.90	17.88	12.02	11.16	0.05	0.42

Chapter 4 - Summary and Conclusions

Vancouver Island

Unlike regions further south, such as the continental shelf and slope of Washington State (Keil et al., 1994b; Mayer, 1994a; Mayer, 1994b), there is no relationship between organic matter preservation and bulk sediment surface area. Organic matter preservation on the continental slope of Vancouver Island is not enhanced by increased bulk sediment surface area, nor does preservation decrease as a result of decreases in sediment surface, therefore other mitigating factors must be acting to allow for organic matter preservation in this region. While sediment supply to the continental shelf and slope is low for this region, the controlling factor upon enhancement of organic matter preservation is likely to be the existence of a sub-oxic intermediate layer of water impinging on the continental shelf and slope, thereby reducing the chance of expedited organic matter degradation.

Arabian Sea

The continental shelf and slope of the Makran area of the Arabian Sea, much like the continental slope of Vancouver Island, does not display any strong correlation between organic carbon concentration and bulk sediment surface area. Relatively stronger correlations between organic matter and sediment surface area are observed outside the oxygen minimum zone, when compared with the relationship between organic

carbon and sediment surface area within the oxygen minimum zone. Thus, outside the oxygen minimum zone sediment surface area appears to have a role in preservation of organic matter, however based on the correlation coefficient between organic carbon concentrations and bulk sediment surface area, the role organic matter adsorption plays in enhancing preservation is minor.

While there was no unequivocal relationship between organic matter preservation and bulk sediment surface area, the samples analyzed were found to be within the monolayer equivalence range as defined by Mayer (1994a; 1994b), however when the fractional coverage was calculated (Mayer, 1999) the sediment surfaces are found to be <20% covered by organic matter. Therefore, based on these calculations the samples can be considered to be coated by discrete patches of organic matter adsorbed onto what has been described by Mayer (1999) as high enthalpy sites, and not adsorbed as a single layer coating the sediment grain surface as previously believed.

The Makran area of the Arabian Sea vs. the coast of Vancouver Island

Both the Makran area of the Arabian Sea and the coast of Vancouver Island are located in tectonically active zones. The Makran area is directly affected by tectonism through re-distribution of sediment via seismic activity and mud-volcanoes resulting from the tectonism (Staubwasser and Sirocko, 2001). The coast of Vancouver Island does undergoes some tectonic events causing re-distribution of sediment via turbidity currents (Mckay, 2003). Along the coast of Vancouver Island bottom water currents have been suggested to move sediments along the shelf and slope destroying the original sediment

distribution regime, whereas in the Arabian Sea sediment re-distribution has primarily been attributed to tectonism.

The sediments found in the Makran area of the Arabian sea have been found to be distributed via aeolian means and via rivers, similarly the sediments found along the Vancouver Island coast were distributed via riverine and aeolian sources, however the Vancouver Island sediment are considered "relict" sediments that were distributed to the continental shelf and slope a long time ago and have undergone re-suspension and re-distribution over time. Modern sediment is rarely distributed to the shelf and slope via coastal riverine sources as the coast of Vancouver Island has extensive fjord systems that act to trap riverine sediments.

Upwelling drives organic matter production in both the Makran area of the Arabian Sea and along the coast of Vancouver Island. Organic matter production in the Arabian Sea is much greater than along the coast of Vancouver Island, the difference in production could be related to the difference in concentration of organic matter preserved as suggested by Calvert and Pedersen (1992).

Future Work

The current study was focused on the relationship between organic matter and bulk sediment surface area. While there was little evidence that the sediment surfaces had any relationship with organic matter in both the Makran area of the Arabian Sea and the continental slope along the southwestern coast of Vancouver Island, there is irrefutable evidence gathered by Mayer (1994a), Mayer (1994b), Keil et al. (1994b),

Hedges and Keil (1995a), Ransom et al. (1997), Ransom et al. (1998), Cowie et al. (1999), Mayer (1999), Arnarson and Keil (2000), Baldock and Skjemstad (2000), Bock and Mayer (2000), Adams and Bustin (2001), and Arnarson and Keil (2001) that organic matter appears to have some relationship with sediment surface areas. Future work in both the Makran area of the Arabian Sea and the southwestern coast of Vancouver Island should include separation of the samples into size fractions for similar analysis to that which was employed for this study. As a result of the re-suspension and re-distribution of sediment and there is possibility that there has been dilution of sediment that have a sediment surface area-organic matter relationship by sediment with little to no relationship. Therefore, there is a probability that any relationship between sediment surface area and organic matter would not be evident when using bulk sediment surface area analysis. By segregating the samples based on their size fractions it may be possible to determine if the organic matter is associated with a specific grain size fraction or if there is no relationship at all between surface area and organic matter for these regions.

Additionally, this study looked at total organic carbon concentrations, which includes both particulate organic matter and dissolved organic matter, however, this study did not discriminate between the particulate and dissolved forms of organic carbon, nor did this study seek to determine to what extent these two forms were associated with mineral surfaces. Some particulate organic matter was observed under the microscope to have no association with adsorption onto mineral surfaces, consequently the question arises: could particulate organic matter that is not adsorbed onto mineral surfaces be masking any surface area-organic matter relationship? Future studies of both the continental slope of southwestern Vancouver Island and the Makran area of the Arabian

Sea endeavor to remove any particulate organic matter that is not adsorbed onto mineral surfaces so as to distinguish if the particulate organic matter that is not associated with mineral surfaces is or is not masking any surface area-organic matter relationship.

In addition, as noted in Chapter 2, the sediments from the continental shelf and slope of Vancouver Island have been classified as relict deposits, getting re-suspended and re-distributed across the continental shelf and slope. There is some question as to whether the action of sediment re-distribution plays a role in masking any surface area-organic matter relationship. As previously stated, re-suspension and re-distribution of sediment grain with adsorb organic matter could result in: 1) the adsorbed organic matter being exposed to condition by which the microbial degradation could occur; and or 2) that grain being re-sedimented into depositional environment where the surrounding sediments have no organic matter adsorbed onto their surfaces thereby the association between that very sediment grain and the adsorb organic matter is masked by the lack of relationship between sediment surfaces and organic matter in surrounding grains. For those reasons, further studies of regions that have relict type deposits, as in the North Sea, might prove to be prudent to determine if there is any association between relict deposits and a lack of correlation between sediment surface area and organic carbon.

Finally, future studies should look closer at how organic matter is adsorbed onto mineral surfaces, whether the organic matter is adsorbed in discrete patches at high enthalpy sites as suggested by Ransom et al. (1997) and Mayer (1999) or if the theory of monolayer adsorption is still applicable. Further energy of adsorption studies and transmission electron microscopy studies on a more diverse sample suite could determine how applicable the latest theory of adsorption in discrete patches is. Furthermore, the

diagenesis of organic matter should be modeled taking into account all the variables that have been found to have some affect on organic matter preservation, thereby giving a big picture view of how organic matter is preserved.

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Appendix 1 - Methods

Total Carbon & Total Nitrogen

Total carbon and total nitrogen were determined using flash-combustion gas chromatography on a Carlo-Erba NA 1500 CNS elemental analyzer.

Dried samples were homogenized using an agate mortar and pestle and then weighed out on a microbalance. A zeroed 8 X 5 mm tin cup was filled with approximately 15 to 30 mg of the dried homogenized sample. Using forceps the tin cup was closed and shaped into an approximate sphere shape. Each sample was placed into a sample tray after final weighing.

Samples were then placed into an AS200 Autosampler that distributed the samples into the analyzer. The samples in the tin cups were flash combusted in a stream of oxygen and helium at temperatures greater than 1800°C. The products of combustion then pass through a column of granulated chromium trioxide (Cr_2O_3) overlying silvered cobaltous cobaltic oxide ($\text{CO}_3\text{O}_4 + \text{Ag}$) maintained at a temperature of 1050°C. This column acts as a catalyst to oxidation of the products of the flash combustion step. Any excess oxygen is removed by passing the stream of gas through heated copper at a temperature of 650°C, which acts to reduce the nitrogen oxides to N_2 . The gas separation is done on a Porapak QS chromatograph column kept at a temperature of 54°C. Individual gases are detected by their thermal conductivity.

For every run of samples three different standards and blanks were used to determine proper operation of the analyzer: sulfanamide; MESS; and BESS. Sulfanamide

is a carbon rich synthetic standard of known carbon and nitrogen concentration. MESS and BESS are both marine sediment standard, also with known carbon and nitrogen values. The standards were weighed out using the same procedure outlined previously for samples and were run before during and after each sample run.

After the analysis was completed, the sulfanamide standard and blank cups were used to create linear regressions using the least-squares method whereby plots were made of both carbon and nitrogen versus area counts. The following algorithms from Verardo et al. (1990) were utilized to calculate the total carbon content [Equations 1, 2, and 3] and total nitrogen content [Equations 4, 5, and 6] of the samples:

$$A_{\text{COR}} = A_{\text{TOT}} - A_{\text{BL}} \quad (1)$$

$$M_{\text{C}} = (A_{\text{COR}}) \times (S) \quad (2)$$

$$\%C = (M_{\text{C}} \div M_{\text{S}}) \div 10 \quad (3)$$

$$A_{\text{COR}} = A_{\text{TOT}} \quad (4)$$

$$M_{\text{N}} = (A_{\text{COR}}) \times (S) \quad (5)$$

$$\%N = (M_{\text{N}} \div M_{\text{S}}) \div 10 \quad (6)$$

where A_{COR} is the corrected area counts of a sample, A_{TOT} is the area counts of a sample, A_{BL} is the area counts of the blank, M_{C} is the mass of total carbon in μg , M_{N} is the mass of total nitrogen in μg , S is the slope of the standard calibration curve, M_{S} is the mass of the sample in mg, $\%C$ is the weight percent total carbon, and $\%N$ is the weight percent of total nitrogen.

Inorganic Carbon

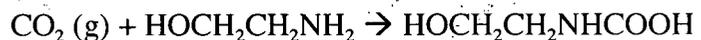
Inorganic carbon was determined using a UIC Coulometrics CO₂-coulometer. Samples were weighed out on a Mettler H20 balance in glass weighing vessels, which were inserted into a larger test tube for analysis. The sample tube was then attached to the acidification module of the coulometer where it was purged of CO₂ for approximately 2 minutes.

The acidification module consists of two air scrubbers: a potassium hydroxide scrubber and a silver scrubber. Air, used as the carrier gas, is pumped into the potassium hydroxide scrubber, which removes CO₂. Once the CO₂ is removed the carrier gas passes into the sample chamber where it carries newly evolved CO₂, the product of the reaction created from the input of 5 ml of 10% HCl to the sample tube, out of the sample chamber and through the second scrubber, the silver scrubber.

The silver scrubber contains a solution of silver nitrate, which is acidified to a pH of 3. This scrubber removes any unwanted gases that are produced as a result of the acidification process that may create abnormal CO₂ values.

Once the gas has left the silver scrubber it enters the cathode cell where it reacts with the cathode solution changing the transmittance of the cathode solution. The following chemical reactions summarize what happens as a result of the CO₂ input into the cathode cell.

1. Adsorption of CO₂ by cathode solution (cathode reaction).



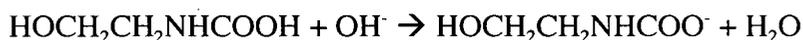
$\text{HOCH}_2\text{CH}_2\text{NH}_2$ ---- monoethanolamine

$\text{HOCH}_2\text{CH}_2\text{NHCOOH}$ ---- hydroxyethylcarbamic acid

2. Electrochemical generation of hydroxide ion (cathode reaction).



3. Neutralization of adsorbed CO_2 reaction produced by electrochemically generated hydroxide ion.



4. Anode Reaction.



The formation of $\text{HOCH}_2\text{CH}_2\text{NHCOOH}$ results in a colour change of the cathode solution from deep blue to colourless, therefore changing the transmittance of the cathode solution. The coulometer then measures the time it takes for the cathode solution to return to its original transmittance, this time is then integrated, by the coulometer, to give a carbon content readout of the sample in micrograms (μg). The typical sample analysis lasts approximately 9 minutes, not including the time it takes to purge the system of CO_2 .

Upon start up of the coulometer blanks are run, using the procedure described above. Samples and standards are not run until a consistent and stable blank of less 10 μg C is achieved. Also, prior to, during and after running any unknown samples, standards of reagent grade carbonate were run to confirm proper operation of the system.

The recorded CO_2 content of each sample was then corrected for background CO_2 using the formula:

$$\% \text{ Inorganic Carbon} = ((\text{Measured}[\text{CO}_2] (\mu\text{g}) - \text{Blank} (\mu\text{g}))/\text{mass of sample} (\mu\text{g})) \times 100\%$$

Organic Carbon

The organic carbon content of each sample was determined using the difference between the total carbon, from flash combustion gas chromatography, and the inorganic carbon content, from coulometry, given by the formula:

$$\% \text{ Organic Carbon} = \% \text{ Total Organic Carbon} - \% \text{ Inorganic Carbon}$$

The % organic carbon is then converted into mg organic carbon per g of sample using the following formula:

$$\text{mg Organic Carbon / g Sample} = (\% \text{ Organic Carbon} / 100\%) \times (1000 \text{ mg} / 1 \text{ g})$$

The resultant value is the total organic carbon content.

Organic Matter Oxidation

In order to determine the available surface area for organic matter to adsorb onto for the bulk sediment, samples were subjected to organic matter oxidation. Current literature, with regards to removal of organic matter from both soils and sediment,

indicate that there are three methods of organic matter oxidation that are widely used in various fields of study: (1) using 30% hydrogen peroxide; (2) using a mixture of sodium pyrophosphate and 30% hydrogen peroxide; and (3) using sodium hypochlorite. For this thesis these three methods were tested to determine which was the most efficient method at removing organic matter from the sediment samples, Appendix 2.

Both the straight hydrogen peroxide method and the sodium hypochlorite method showed residual organic carbon content that was greater than can be explained by analytical error. Furthermore, the sodium hypochlorite in method (3) reacted with the manganese in some samples forming permanganate, whilst the 30% hydrogen peroxide method appeared had no cessation of CO₂ evolution, and therefore the hydrogen peroxide was concluded to be reacting with inorganic mineral matter. The method using a combination of sodium pyrophosphate and hydrogen peroxide removed the organic matter more effectively than the other methods and appeared not to be reacting with the sediment in the same manner as either of the other methods.

The oxidation solution for the sodium pyrophosphate method used was prepared in 1L batches using the procedures of Sequi and Aringhieri (1977) as a guide. Approximately, 44.605 ± 0.005 g of sodium pyrophosphate was precisely weighed and added to 1 L of distilled water making a 0.1 M solution of sodium pyrophosphate. Then using a graduated cylinder 800 ml of 0.1 M solution was added to a 1 L Nalgene[®] bottle. Using another clean graduated cylinder 200 ml of 30 % hydrogen peroxide was measured and added to the same 1 L Nalgene[®] bottle as the sodium pyrophosphate. A stir bar was dropped into the bottle and the mixture was stirred for 5 minutes. The sodium

pyrophosphate and hydrogen peroxide mixture were then stored in the 1 L Nalgene[®] bottle.

Approximately 6 g of dry sediment was added to a 600 ml beaker containing 200 ml of distilled water. In a graduated cylinder, 20 ml of the 0.1 M sodium pyrophosphate and 30% hydrogen peroxide solution was measured and then added to the beaker. The beaker was then placed in a sonic bath for 5 minutes to disaggregate any large clumps of clay that may have formed during the initial freeze-drying step. The beaker was then transferred into a water bath that was held at a constant temperature of $75^{\circ}\text{C} \pm 5^{\circ}\text{C}$. Samples were treated every 6 to 8 hours with 20 ml aliquots of the sodium pyrophosphate and hydrogen peroxide solution. This process was carried out until the cessation of CO_2 evolution, typically 48 to 96 hours. Some samples were tested to make sure that indeed the organic carbon was fully oxidized.

With the organic matter fully oxidized samples were then cleaned via a process of centrifuging the samples to separate the sediment from liquid. The liquid was poured off, and then the samples were rinsed three times with distilled water and centrifugation after each rinsing.

Carbon Stable Isotope Analysis

Freeze dried samples were finely ground using an agate mortar and pestle. The ground samples were then treated with 10% Environmental Grade hydrochloric acid to remove inorganic carbon. The samples were then dried at a constant temperature of 50°C and are weighed into tin cups. Each filled sample cup was pressed to remove air and then

was placed into an AS 128 autosampler along with several lab standards. Samples were analysed using a Carlo Erba Instruments Thermoquest NC 2500 elemental analyzer.

The autosampler releases each into the analyzer where enters a combustion column that is set to a constant temperature of 1020°C, this column is packed with chromium oxide and silvered cobaltous oxide. At the moment the sample enters the combustion column a pulse of ultra high purity (UHP) oxygen is released into the column to combust the sample forming NO_x , CO_2 and H_2O gases. The gases are then transported to the reduction column via UHP helium. The reduction column is packed with copper wire and set a constant temperature of 750°C. Within the reduction column the NO_x gas gets converted to N_2 gas.

After the reduction column sample gases pass through magnesium perchlorate, which traps and removes any water.

Cleaned of water, the sample then passes through a gas chromatograph column that separates the N_2 gas from the CO_2 gas. The separated gases leave the elemental analyzer and are carried to an open slit of a Finnigan, Conflo III where the sample gas is taken up via a fine capillary attached to the Finnigan, Delta Plus mass spectrometer.

Within the mass spectrometer the gas is carried to the source where the molecules are bombarded with electrons and converted to positively charged ions. The ions are accelerated down a tube deflected by a magnet towards a universal detector cup. The detector detects masses 44, 45 and 46 for CO_2^+ . Using ISODAT software ratios of masses 45/44 are compared to the relative ratio of the CO_2 reference gas, thus determining the isotopic value of the sample.

The isotopic value is then further corrected by plotting a calibration curve of expected isotopic values versus measured isotopic values for various lab standards, which are analysed throughout the sample run. The various lab standards have been calibrated against international NBS19 (+1.95 per mil), NBS20 (-1.06 per mil) and NBS21 (-28.10 per mil).

Surface Area

Surface area was determined using a Micromeritics® ASAP 2010 surface area analyzer by N₂ adsorption using multi-point BET (Brunauer, Emmett, Teller) method. Surface area analysis was applied to some samples both prior to and after organic matter oxidation, whilst some samples were only analysed post-organic matter oxidation.

Weighed samples were put into glass sample tubes, supplied by Micromeritics®, and degassed at a constant temperature of 120°C for 3 – 4 hours, or until the pressure dropped below 12 µmHg. Degassing was done to remove any water or gases, which may be trapped on the surface or within internal surfaces of mineral grains. Any residual water and or gases may inhibit proper operation of the surface area analyzer. Following degassing samples were analysed using nitrogen as the sorbate at liquid nitrogen temperatures. The ASAP 2010 surface area analyzer software was set up to take measurements at 5 pressure steps, which would then be integrated with the assistance of the ASAP 2010 software to produce the total bulk sediment surface area, along with other parameters such as pore size and micro-pore surface area.

A silica-alumina standard provided by Micromeritics® was used periodically during the operation of the surface area analyzer to determine if the machine was operating properly. The standard was typically used prior to and after long runs, as well as during the operation to confirm the validity of the data.

Appendix 2 - Organic Matter Oxidation Method **Experiment**

Introduction

Prior to any physical, chemical and mineralogical analyses of soils and sediments, hydrogen peroxide has typically been used to oxidize the sedimentary organic matter (Lavkulich and Wiens, 1970; Sequi and Aringhieri, 1977). Hydrogen peroxide does have an affinity for oxidizing organic matter, though peroxide also has been found to have deleterious effects on the inorganic material found in both sediments and soils that can have potential have affects on data from physical, chemical and mineralogical analyses of soils and sediments. Studies in the field of soil sciences have found that peroxidation of samples can result in mica exfoliation (Drosdoff and Miles, 1938), as well the formation of calcium oxalate (Martin, 1954). Furthermore, the ability of hydrogen peroxide as an efficient organic matter oxidizing agent has been put into question (Drosdoff and Miles, 1938; Martin, 1954; Lavkulich and Wiens, 1970; Sequi and Aringhieri, 1977).

Anderson (1963) developed a procedure using sodium hypochlorite as an oxidizing agent for organic matter as salts of hypohalous acids typically did not produce the same undesirable effects that had been observed as a result of hydrogen peroxide oxidation. Anderson (1963) and Lavkulich and Wiens (1970) both site the major advantages of using sodium hypochlorite is the rate at which oxidation of organic matter occurs and that the sodium hypochlorite had little, if any, affect on the inorganic material in their samples (Lavkulich and Wiens, 1970). The inertness of this method with respect

to the inorganic material in soils and sediments is what makes this method ideal in preparing samples for further analyses (Lavkulich and Wiens, 1970).

Another method that has proven to be reliable in removing organic matter is the method described by Sequi and Aringhieri (1977), which uses a solution containing both hydrogen peroxide and sodium pyrophosphate. This method has been utilized successfully, with no reported affects to the sediment samples, in many studies related to soil and sediment specific surface area for the preparation of samples prior to BET analysis (Mayer, 1994a; Mayer, 1994b; Ransom et al., 1997; Ransom et al., 1998; Mayer, 1999; Adams and Bustin, 2001; Mayer et al., 2002).

In order to determine the most efficient method by which organic matter could be removed from the inorganic material for this thesis, the three methods were evaluated: (1) the hydrogen peroxide method (Sequi and Aringhieri, 1977); (2) the sodium hypochlorite method (Lavkulich and Weins, 1970)(Anderson, 1963); and (3) the sodium pyrophosphate and hydrogen peroxide method (Sequi and Aringhieri, 1977).

Materials and Methods

Surface samples of varying total organic carbon concentrations from the Makran area of the Pakistani continental shelf and slope were chosen to undergo the three different organic matter oxidation procedures. These surface core samples were the most organic rich samples for the Makran. The samples were obtained during the PAKOMIN, Pakistan-oxygen-minimum-zone, study of sediments on the Pakistan margin in 1990 on

the German research vessel FS Sonne. The box cores were obtained via a Kasten box-corer, sub-sampled and stored at -20°C in a freezer until being freeze dried.

Approximately 5.0 g of dry sample was placed into a 600 ml beaker containing 200 ml of distilled water, this process was repeated a total of 12 times such that each surface sample would be undergo organic matter oxidation by each method of oxidation. The beakers were then placed into a sonic bath for 5 minutes to disaggregate any large sediment masses that may have occurred during the freeze drying process. After the disaggregating step, samples were placed in a water bath that maintained a temperature between 70°C and 80°C then subject to organic matter oxidation.

Hydrogen Peroxide Method

The hydrogen peroxide method consists of adding aliquots of 1 ml of 30% hydrogen peroxide for every 10 ml of water in the beaker. After the first aliquot of peroxide is added the beaker is left in the water bath to allow for oxidation to occur. Once CO_2 evolution appears to cease the distilled water is added to the beaker to maintain the original 200 ml level. Another aliquot of 20 ml of 30% hydrogen peroxide is added to the beaker, if the CO_2 evolution occurred the sample is left in the water bath and this step is repeated until the cessation of CO_2 evolution.

Once the organic matter is fully oxidized, the samples are then transferred to centrifuge tubes and centrifuged. The supernatant is poured off and the samples are then rinsed three times with distilled water with centrifugation and decanting occurring in between each rinsing.

Sodium Hypochlorite Method

The sodium hypochlorite method consists of adding an initial aliquot of 20 ml of sodium hypochlorite solution (minimum 6% available chlorine (Lavkulich and Wiens, 1970)) to the sample. The sample is then left in a water bath set to a temperature ranging between 70 and 80°C. The sample is allowed to sit in the water bath for approximately 15 minutes. After 15 minutes, the supernatant is poured off, the distilled water is topped up to the 200 ml level and another 20 ml aliquot of sodium hypochlorite is added. This process is repeated a total of 5 times, after the fifth treatment the samples were then rinsed three times with distilled water, with centrifugation occurring between each rinsing.

Upon noticing the supernatant turning pink in colour the supernatant was saved. Excess liquid was evaporated from the supernatant by putting it into an oven set to 50°C and leaving it to sit until there was no liquid remaining. The residue was then treated for the purpose of XRD analysis.

Sodium Pyrophosphate and Hydrogen Peroxide Method

Treatments begin with mixing a solution that consists of 800 ml of 0.1M sodium pyrophosphate and 200 ml of hydrogen peroxide. The solution is then distributed to the samples in 20 ml aliquots. After the first aliquot of sodium pyrophosphate solution the sample is stirred and is left in the water bath to allow the oxidation reaction to occur, typical reaction took between 48 and 96 hours (Adams and Bustin, 2001). Upon cessation of frothing and CO₂ evolution the treatment is again repeated until no reaction could be observed, CO₂ evolution subsided.

With the organic matter oxidation reaction finished the samples are then transferred to centrifuge tubes and centrifuged. The supernatant is pour off and the samples are rinsed three times with distilled water with centrifugation and decanting occurring in between each rinsing.

Organic Carbon Concentrations

Once the samples had undergone the various organic matter oxidation methods they were evaluated for their organic carbon concentrations. The samples were freeze dried to remove any excess water. The dried samples were then analyzed for total carbon using flash-combustion gas chromatography on a Carlo-Erba NA 1500 CNS elemental analyzer. The operation of the analyzer and composition of the combustion column are similar to those described by (Verardo et al., 1990). As, well the samples were analyzed for their inorganic carbon concentrations using a UIC Coulometrics CO₂-coulometer. Samples were dosed with 10% hydrochloric acid, which reacts with the carbonate in the sample forming CO₂. The CO₂ is carried to the coulometer where it is quantified and integrated giving the inorganic carbon content. The difference between the total carbon concentration and the inorganic carbon concentration is the organic carbon concentration.

Results And Discussion

All three methods for organic matter oxidation worked with varying degrees of success. By far the most consistent and effective method is the sodium pyrophosphate method. Depending on the sample, between 89.2% and 97.7% (Table 1; Figure 1) of the organic matter was removed by this method. Whereas, the sodium hypochlorite method

and the hydrogen peroxide method removed between 21.9%-88.9% and 85.7%-117.4% (Table 1; Figure 1) of the organic matter, respectively.

While the hydrogen peroxide method proved to successfully remove a majority of the organic matter from the samples, there appeared to be a secondary reaction occurring. After successive additions of hydrogen peroxide there was some violent fizzing that was not characteristic of the reaction between the hydrogen peroxide and organic matter previously seen during other organic matter oxidations using the same hydrogen peroxide method. As these samples contain weathered clay minerals such as micas, chlorite, and smectite there is a possibility that the violent fizzing observed may be related to the exfoliation reaction described by Drosdoff and Miles (1938). Drosdoff and Miles (1938) found that when weathered mica were treated with a few milliliters of 30% hydrogen peroxide the micas gradually began to exfoliate and when the exfoliated micaceous particles were analyzed via X-ray diffraction they no longer resemble mica in a diffractogram, rather they had properties of vermiculite.

The sodium hypochlorite method has a less violent reaction than the other two methods and the oxidation process was much quicker than the other two methods, samples could be oxidized in under a day. The downside to this method was that there appeared to be incomplete oxidation of the organic matter, sample 1 KG 0-5 had only 21.9% of the organic matter removed. Furthermore, the supernatant became a brilliant pink colour during the process, while this observation was not record by Lavkulich and Wiens (1970), Anderson (1963) made a note of a similar occurrence in his study, however he never identified the make up of the pink supernatant. X-ray diffraction analysis of the salts left behind via evaporation of supernatant showed an appreciable

manganese oxide peak. Given the colour of the supernatant and the diffraction pattern it is possible that the supernatant is permanganate.

The sodium pyrophosphate method removed the most organic matter, when compared with the other organic matter oxidation methods, however the sodium pyrophosphate method had a similar problem as the hydrogen peroxide method. After the fourth or fifth aliquot of the sodium pyrophosphate and hydrogen peroxide solution the contents of the beaker began to react almost as violently as seen in the hydrogen peroxide method. The reason for this secondary reaction is similar to that given for the hydrogen peroxide method.

Conclusion

While all the organic matter oxidation steps studied are accepted procedures to destroy organic matter in both sediments and soils for the purposes of chemical and physical analysis, the sodium pyrophosphate method described by Sequi and Aringhieri (1977) is the most effective organic matter oxidation method. All three organic matter oxidation methods appeared to have secondary reactions, which have not been fully explained in previously literature. Future studies of the sodium pyrophosphate method should be done to determine at what point the organic matter oxidation has been completed, as well at what point the secondary reaction occurs.

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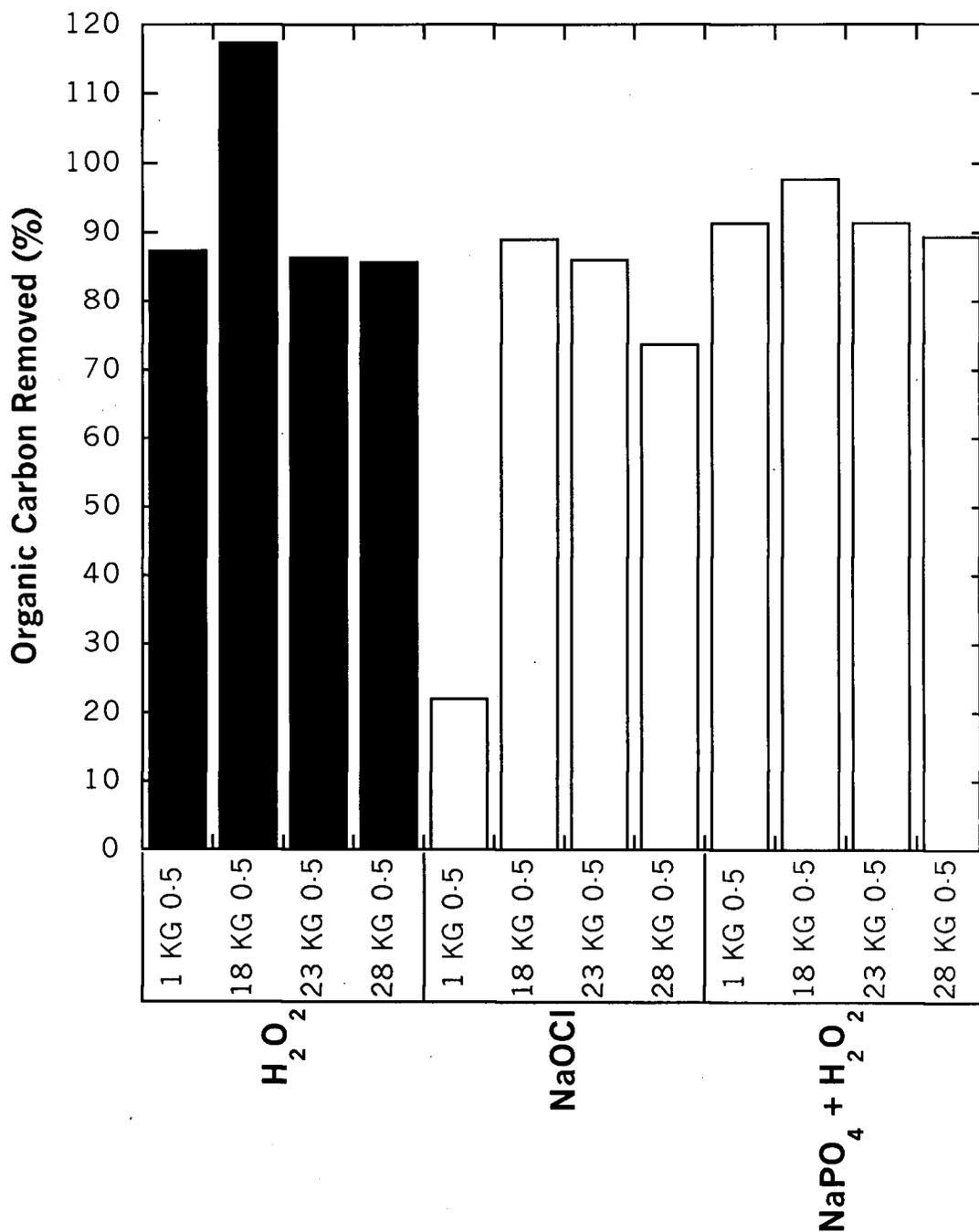


Figure 1: Graph showing the percentage of organic matter removed from a series of samples using the three methods of organic matter oxidation: the peroxide method, H_2O_2 ; the sodium hypochlorite method, $NaOCl$; and the sodium pyrophosphate/hydrogen peroxide method, $NaPO_4 + H_2O_2$.

Table 1: Comparison of each method of organic matter oxidation for a series of surface samples from the Makran area of the Arabian Sea. The peroxide method, H_2O_2 , the sodium hypochlorite method, NaOCl, and the sodium pyrophosphate/hydrogen peroxide method, $Na_2P_2O_7 + H_2O_2$.

Oxidation Method	Sample	Un-oxidized Organic Carbon (%)	Organic Carbon After Oxidation (%)	Organic Carbon Removed (%)
H₂O₂	1 KG 0-5	0.65	0.08	87.4
	18 KG 0-5	1.11	-0.19	117.4
	23 KG 0-5	1.36	0.19	86.2
	28 KG 0-5	2.47	0.35	85.7
NaOCl	1 KG 0-5	0.65	0.50	21.9
	18 KG 0-5	1.11	0.12	88.9
	23 KG 0-5	1.36	0.19	85.9
	28 KG 0-5	2.47	0.65	73.7
Na₄P₂O₇ + H₂O₂	1 KG 0-5	0.65	0.05	91.5
	18 KG 0-5	1.11	0.03	97.7
	23 KG 0-5	1.36	0.12	91.2
	28 KG 0-5	2.47	0.27	89.2

Appendix 3 - Organic Matter Oxidation Time Experiment

Introduction

The method chosen for organic matter oxidation throughout this study was the sodium pyrophosphate method described by Sequi and Aringhieri (1977), and outlined in both Appendices 1 and 2. This method was chosen after three common methods for organic matter oxidation were evaluated for their effectiveness in removing organic matter from four surface samples of containing typical continental shelf and slope organic carbon concentrations (Appendix 2). The sodium pyrophosphate method, much like the other two organic matter oxidation methods, had secondary reactions occur during oxidation. In order to minimize any effects from secondary reactions, a time-lapse experiment was setup. A time-lapse experiment would, therefore, show at what point the oxidation of organic matter had ceased, thus minimizing any damage to the inorganic material in the samples.

Materials and Methods

The oxidation solution for the sodium pyrophosphate method used was prepared in 1L batches using the procedures of Sequi and Aringhieri (1977) as a guide, details can also be found in Appendix 1.

Approximately 6 g of dry sediment, sample 28 KG 0-5, was added to each 600 ml beaker containing 200 ml of distilled water. A total of 6 beaker were used, one beaker for every time interval; 24h, 48h, 72h, 96h, 120h, and 168h. In a graduated cylinder, 20 ml of

the 0.1 M sodium pyrophosphate and 30% hydrogen peroxide solution was measured and then added to each beaker. The beakers were then placed in a sonic bath for 5 minutes to disaggregate any large clumps of clay that may tend to form during freeze-drying. The beakers were then transferred into a water bath that was held at a constant temperature of 70°C-80°C. After the initial treatment of the sodium pyrophosphate and hydrogen peroxide solution samples were given additional aliquots of the solution every 12 hours. During the oxidation experiment additional distilled water was added to the beakers to maintain a constant water level of 200 ml in order to keep the samples from drying out.

After 24 hours the first sample, 24h, was removed from the water bath and transferred to centrifuge tubes. The sample was then centrifuged separating the sediment from the supernatant. The supernatant was discarded and the sediment was then rinsed with distilled water and underwent centrifugation again. The supernatant was again discarded and the sediment was again rinsed with distilled water and centrifuged. This process of rinsing and centrifuging was repeated a total of three times. After 48, 72, 96, 120 and 168 hours the same procedure used to clean sample 24h was applied to samples 48h, 72h, 96h, 120h and 168h, respectively. The time series samples were then freeze dried and analyzed for organic carbon concentration determination, as described in Appendix 1.

Discussion

After 24 hours of the sample being subjected to organic matter oxidation approximately 91.7% of the organic matter had been removed from the sample, Table 1.

After 48 hours the amount of organic matter removed is approximately 102.3%, while this seems quite odd that more organic matter was removed than actually was originally measured this value is within reasonable error of 100% organic matter removal. The error in the process of determining organic carbon concentrations is approximately 4%. After 72, 96, 120, and 168 hours the amount of organic matter removed is 94.2%, 94.7%, 99.7%, and 94.1%. Therefore a majority of the organic matter is removed within the first 24 hours of oxidation while 100% of the organic matter, with in the error of the technique, can be considered removed after 48 hours.

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Table 1: Comparison of total carbon, total C, inorganic carbon, IOC, and organic carbon, OC, during a time lapse experiment using the sample 28 KG 0-5 cm from the Makran area of the Arabian Sea.

Sample:	28 KG 0-5 cm					
	% TC =	4.15	% IOC =	1.68	Original % OC=	2.47
Time (hours)	Sample Weight (g)	Total C (after Oxidation) (%)	%IOC (after oxidation)	OC (After Oxidation) (%)	OC Carbon Removed (%)	% Difference (Δ from Before to After Ox.)
24	5.00	2.14	1.94	0.20	91.74	8.26
48	5.02	1.84	1.90	-0.06	102.26	-2.26
72	5.05	2.05	1.91	0.14	94.17	5.83
96	5.07	1.91	1.78	0.13	94.73	5.27
120	4.98	1.78	1.77	0.01	99.74	0.26
168	5.12	1.92	1.77	0.15	94.05	5.95