

THE UNIVERSITY OF LIVERPOOL

**TRACE METALS AND ORGANIC MATTER DIAGENESIS AT
THE OMAN MARGIN**

Thesis submitted in accordance with the
requirements of the University of Liverpool for
the degree of Doctor of Philosophy

by

R. ALAGARSAMY

Oceanography Laboratories, Department of Earth Sciences,
University of Liverpool

SEPTEMBER, 1997

ABSTRACT

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Trace Metals (e.g. Mn and Fe) play an important role as secondary oxidants in the degradation of sedimentary OM under sub-oxic conditions. Hence the remineralisation of organic constituents of sediments in the marine environment may significantly control the diagenetic behaviour of a number of trace metals and their cycling and subsequent release to overlying waters. Although, these reactions have been investigated thoroughly in marine sediments, their relationship with the diagenesis of OM has not been directly established. Hence, a study of the diagenesis of OM and trace metals in sediments from the Oman Margin (Arabian Sea) has been undertaken in order to gain an understanding of the relationship between the biogeochemistry of OM and redox-sensitive trace metals. To the best of the knowledge of this author, few recorded studies of trace metal speciation and its association with organic matter in Arabian Sea sediments exist. This study is the first of its kind of organic-rich sediments and attempts to assess the manner in which the degradation of individual organic components affects the solid state speciation of trace metals in the sediments of the Oman Margin (Arabian Sea). To this purpose, two 'diagenetically-active' sediment cores from the Oman Margin (abyssal site) and three replicate sediment cores from the shallow environment i.e. most intense part of the OMZ site have been analysed for trace metals Fe, Mn and Cu along with OM constituents such as TOC, TN, THAA and THCH and other bulk parameters. Data for all these are presented in an appendix. The abyssal sediments chosen for this study were influenced by a sandy turbidite, having 3 units on the basis of their sedimentology and geochemistry. The solid state speciation of the non-detrital fractions revealed that Mn spike is a classic feature in the diagenesis of Mn, and the present study has shown that it is composed of 'new' Mn₃ oxides. There are no other clearly defined relationships in the solid state speciation of 'aged' oxides of Mn₄, Fe₄ and Cu₄ that can be defined as being diagenetically-mediated. There was ***no*** relationship between OM parameters and Mn (or Fe) solid state speciation, presumably reflecting the complete removal of 'new' oxides from the deeper sediments.

The shallow environment of the most intense part of OMZ sites contrasted with the abyssal sites. There was no detectable non-detrital Mn in these cores due to the lack of Mn₃ 'new' oxides precipitation in surficial sediments and the reduction and export of any Mn₄ 'aged' oxides. There were no other clearly defined relationships in the solid state speciation of 'aged' oxides of Fe₄, that could be defined as being diagenetically-mediated. Differences in OM parameters were linked to the distinct compositions of the cores and the sources of the OM to the cores were complex. Surprisingly, and in contrast with other productive environments such as the Peru Margin, there was little apparent diagenetic modification of OM with increasing sediment depth. There was ***no*** relationship between OM parameters and Mn (or Fe) solid state speciation, presumably reflecting in part the low diagenetic activity.

DEDICATED
TO
MY LOVING PARENTS

ACKNOWLEDGEMENTS

I am extremely indebted to my supervisors Prof. Roy Chester and Dr. George A. Wolff for their valuable direction, advice and encouragement throughout the duration of this research. Their endless support, patience and understanding have aided me considerably to carry out this work to the best of my ability and preparation of this thesis.

I would also grateful to Mrs. Paula Houghton, Doris Angus, Carmel Murphy, Jane Barnard, Hilda, Alan, David Whithead, Ian Carr and Vaziri for their technical support. I also offer my warm thanks to Danny Boardman and Sarah for their help in computing, and Dr. Anu Thomson and Prof. Roger Wilson for reading my draft. I acknowledge my thanks to the friendship, advice and help of all colleagues from various quarters and staff in the department for their valuable assistance.

I am particularly grateful to my parents, wife Mrs. Beula, and my loving daughters Priyadharsini and Nithiya for their encouragement, patience and understanding during the period of study. It is my pleasant duty to tender my grateful acknowledgements for valuable help received from my brothers Mr. R. Gunasekaran and Mr. R. Duraikannan, and sister Mrs. Santhi.

I would like to thank the Government of India for financial support, the High Commission of India for their help and the National Institute of Oceanography, Goa/CSIR, New Delhi for granting my study leave.

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CHAPTER 1 - INTRODUCTION

1.1. Deep Sea Sediments

The ocean covers most of the surface of the Earth (71%), averaging 3730 metres (12,200 feet) depth. The study of the world ocean plays a major role in the understanding of various aspects of the physics and chemistry of the Earth. From the chemical viewpoint, the oceans act as a major reservoir in global geochemical cycles. In particular, marine sediments are the ultimate sink for most of the material derived from the continents, either from natural or anthropogenic sources, being transferred to the oceans on a global-scale via riverine and atmospheric transport, with glacial transport and hydrothermal inputs to sediments being important locally. The other important source of sediments is that of material formed by biogenic production in the water column (pelagic production). Much of the deep-sea floor is carpeted with pelagic sediments (i.e. that deposited beyond the continental shelf), which cover ~50% of the Earth's surface.

Sediments are important because they contain a record of past conditions in the ocean and they are, therefore, important proxies for the quantification of the various fluxes contributing to the global geochemical cycles. Studies of deep-sea sediments, can contribute our the understanding of the behaviour of the dissolved and particulate constituents of seawater, both natural and anthropogenic, in the various marine chemical cycles.

1.2. Classification of Marine Sediments

The chemical and physical processes at the earth's surface partially separate the chemical elements into various fractions (Goldschmidt, 1937). The composition of sediments shows great variability from one environment to another as a result of different mechanisms of chemical fractionation. In order to classify the diversity of the sediment components, Krynine (1948) made a distinction between the portion of weathered material transported in a solid form and the portion which remains in solution (or in colloidal suspension) for much of the weathering cycle. Hence, the sedimentary components were classified in a simple two fold scheme; i.e. those of detrital origin, transported in solid form, and those of non-detrital (or authigenic) origin transported as dissolved material.

Goldberg (1954) suggested that the main constituents of marine sediments can be classified into lithogenous, biogenous, hydrogenous and cosmogenous components, on the basis of their origin in the geosphere or outer space (Fig. 1.1). The cosmogenous components, consisting of extra-terrestrial material, do not play a significant role in deep-sea sediments. In addition, Goldberg (1954) identified an aqueous sediment phase, i.e. pore solutions or interstitial waters.

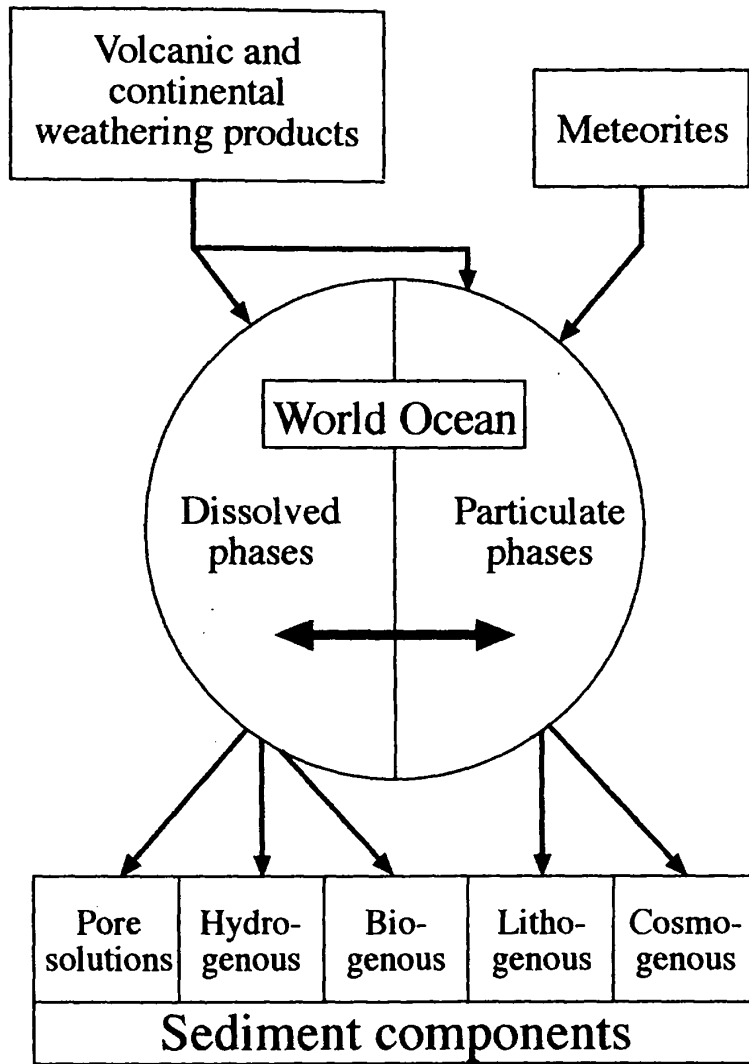


Fig. 1.1. The classification of the components of marine sediments.
 (after E.D.Goldberg, 1954).

1.3. Nature of Trace Metals

An important characteristic of deep-sea sediments is that they contain enhanced (excess) concentrations of certain trace elements, such as Mn, Cu, Ni, Co and Zn. Trace metals entering the marine environment are removed from surface waters by either physical (i.e. water movement) or chemical and biological (scavenging) processes and transported to the sediment surface in a variety of solid phase associations, in the form of biogenic detritus, clay minerals and hydrogenous precipitates. Detrital elements are associated with a crystalline mineral matrix and are usually immobile with respect to early diagenesis. In contrast, elements which have been transported in a dissolved form and have been incorporated into sediments from solution (the non-detrital or non-residual or authigenic fractions) are associated with a variety of non-crystalline phases. The non-residual elements have the potential to be environmentally mobile and can be involved in the particulate/dissolved reactions of the aquatic biogeochemical cycles. During early diagenesis, dissolution, remobilization and migration of trace elements occurs at and below the sediment/water interface; the latter resulting in a supply of trace elements to the upper portions of deep-sea sediments.

1.4. Diagenetic Processes in Marine Sediments

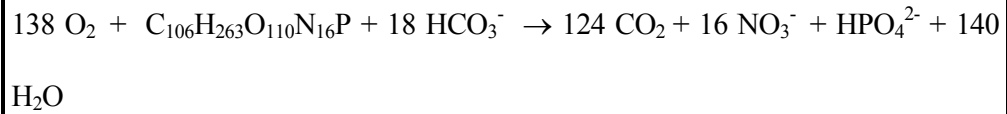
Diagenesis is the term applied to the sum total processes that bring about changes in sediments, or sedimentary rocks, subsequent to deposition (Berner, 1980). Early diagenesis of organic matter (OM) in marine sediments changes the quantity and composition of the OM in the upper several hundred metres of the sediment column (Berner, 1980). The sediment-water interface is an active site for biological, chemical and physical processes which act upon the arrival of particles, and ultimately lead to the formation of new and altered mineral phases and the alteration of the composition of sediment pore-waters. Most early diagenetic changes (i.e. those taking place in the upper few metres of sediments) are driven by redox reactions as a result of oxidation of OM. Hence, sub-oxic and anoxic conditions often prevail in marine sediments and these have a profound effect on the distribution of trace metals.

There is a diagenetic sequence of catabolism in the sediments, which is driven by microorganisms that utilise specific oxidising agents to 'burn' the organic carbon. These oxidising agents are consumed in order of decreasing energy production per mole of organic carbon oxidised (Table 1.1). The diagenetic processes firstly utilize dissolved O₂, then a series of secondary oxidants (electron acceptors), and proceed in the general sequence : oxygen > nitrate > manganese oxides > iron oxides > sulphate (Table 1.1).

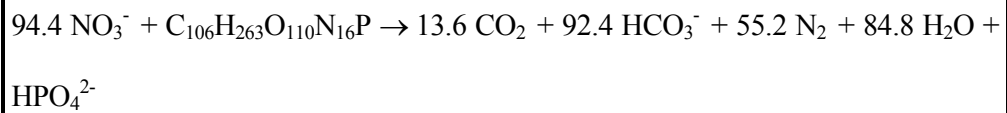
Sedimentary diagenetic processes can be divided, on the basis of the redox potential of the sediment into i) **Oxic** types, in which dissolved oxygen is the oxidant, and ii) **Sub-Oxic** types in which secondary oxidants are used in the diagenetic sequence given in Table 1.1.

Table 1.1. Oxidation reactions of organic matter in marine sediments (Froelich et al. 1979).

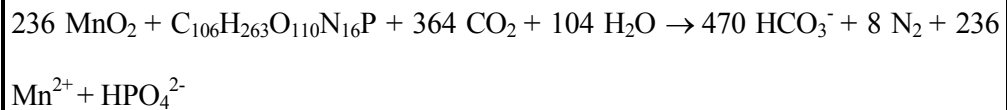
1. OXYGEN REDUCTION



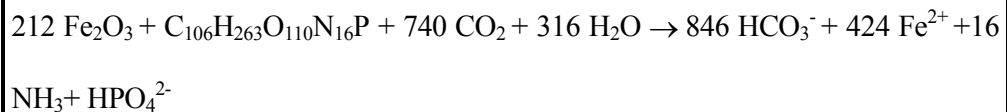
2. NITRATE REDUCTION



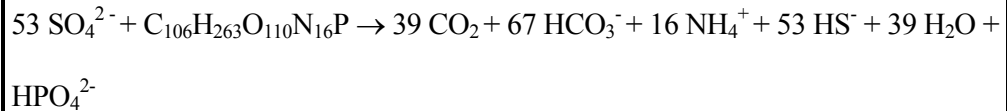
3. MnO₂ REDUCTION



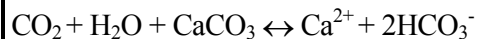
4. Fe₂O₃ REDUCTION



5. SULPHATE REDUCTION



6. CALCIUM CARBONATE DISSOLUTION/PRECIPITATION



The factors which control the extent to which the diagenetic sequence operates are (a) the magnitude of the OM flux to the site of sedimentation (dependent on the degree of primary productivity in the overlying waters), and (b) the rate at which the sediment accumulates. In sediments that are deposited under oxic conditions, organic carbon is rapidly destroyed (with oxygen as an electron acceptor), usually at the sediment-water interface. Bioturbation by metazoans leads to accelerated rates of OM destruction (Aller, 1982), and greatly influences both the nature and vertical distribution of OM in the top centimetres of the sediment column (Mayer, 1993). The surficial sediments are more important to biological fauna compared with sub-surface sediments since meiofauna and macrofauna live above the reduced zone in sediments.

1.5. Role of Trace Metals in Diagenesis

The sediment-water interface plays an important role in the chemistry of trace metals (Luoma and Bryan, 1981). During diagenesis, metals are released from their organic carriers and are enriched in upper interstitial waters. This enrichment can lead to a downward migration of the metals into sediment or an upward migration into seawater. If the dissolved oxygen is exhausted (i.e. high OM deposition and high sedimentation rate), the organic carrier phases and associated metals can be buried, but the former may ultimately be respired via secondary oxidants such as Mn oxides during sub-oxic processes, usually occurring at depth in the sediment column (see Froelich et al. 1979). Microorganisms utilize manganese and iron oxides as oxidants and release Mn^{2+} and Fe^{2+} , and metals associated with these oxide phases, into interstitial waters

(e.g. Hem, 1978; Callender and Bowser, 1980; Klinkhammer et al. 1982; Sawlan and Murray, 1983; Burdige, 1993). The upward/downward diffusion of many of these released metals takes place in response to concentration gradients. Marine sediments contain surface oxic layers which increase in thickness from near-shore to pelagic environments, due to slow accumulation and under the oxidising conditions prevailing in these layers, migrating Mn^{2+} and Fe^{2+} may be reprecipitated near the sediment/water interface, together with some of the other trace metals released at depth in the sediments (Sawlan and Murray, 1983; Heggie and Lewis, 1984).

During early diagenesis in marine sediments, the redox sensitive metals (e.g. Mn, Co, Cu) are transported from the non-residual fraction of reducing sediments to the overlying water, particularly in near-shore continental margin sediments (Duinker et al. 1974; Sundby et al. 1981; Trefry and Presley, 1982; Martin and Whitfield, 1983; Chester, 1990; Silverberg and Sundby, 1990), and also in pelagic sediments, where diagenetic Mn and associated polymetallic nodules are formed (Sundby et al. 1981; Trefry and Presley, 1982; Silverberg and Sundby, 1990). In this respect, manganese and copper are of particular interest, as they exhibit distinct redox-mediated reactions due to their occurrence in different carrier phases in sedimentary particulate material. The following sections will describe in more detail the reactions of these metals in the marine environment.

1.5.1. Manganese

Manganese is the eleventh most abundant element in the Earth's crust (Glasby, 1984). It is utilised as an essential micronutrient by all organisms. In natural waters, Mn exists as insoluble Mn (II and IV) oxides and as soluble Mn (II) ions. Manganese is a 'scavenging-type' element in sea-water; i.e. in the dissolved form it exhibits a surface enrichment and decreases in concentration with increasing depth in the absence of mid-depth sources (e.g. Whitfield and Turner, 1987 and Chester, 1988). Manganese associated with inorganic carrier phases is scavenged from the water column before it reaches the sediment surface (e.g. Dymond, 1984; Chester, 1990). Much of this manganese is transformed to oxides at the sediment surface (e.g. Lyle et al. 1984; Thomas, 1987; Chester et al. 1988), before being buried as the sediment accumulates. These oxides are preserved in the sediments under oxic conditions. However, under reducing conditions, they can be utilized as secondary oxidants for the respiration of any organic carbon which has escaped initial destruction at the sediment surface. As this happens, the reduced manganese is released into solution as Mn^{2+} , and migrates up the sediment column via an interstitial water concentration gradient, to be re-precipitated in the upper oxic layer of the sediments (e.g. Froelich et al. 1979 ; Burdige and Gieskes, 1983).

A number of steady state, coupled, non-linear models have been developed for early diagenetic processes in pelagic and hemi-pelagic marine sediments. That of Dhakar and Burdige, (1996) proposes that the occurrence of the oxic and sub-oxic diagenetic processes is significantly affected by variations in parameters such as the sedimentation rate, bioturbation coefficient, sediment porosity, and

OM flux to the sediments. During sub-oxic processes, the oxidation of OM is increased either due to sedimentation rate, or the bioturbation coefficient. The OM oxidation by sub-oxic processes decreases with an increase in sediment porosity.

Early diagenesis in marine sediments can occur:

- 1) under steady state conditions, in which the redox boundary moves upwards in relation to sedimentation rate (Lynn and Bonatti, 1965; Froelich et al. 1979).
- 2) under non-steady state conditions, where the redox boundary moves downwards because of the trapping of oxidants resulting from turbidite deposition on pelagic sediments (Colley et al. 1984; Wilson et al. 1986) or from changes in oceanic fertility (Berger et al. 1983; Thomson et al. 1984). The respiration of OM and immobilisation of diagenetically-sensitive metals in the redox front (Colley et al. 1984; Buckley and Cranston, 1988) has been reported in the non-steady state sediments.

Model results show that the internal redox cycling of manganese in sediments leads either to the formation of a Mn-peak near the sediment redox boundary (e.g. Fig.1.2), or to surficial Mn-rich oxic sediments, depending on depth zonation of manganese oxidation and the degree of bioturbation. In sediments with a shallow redox boundary (<5 cm), upward diffusion of pore water manganese into the oxic sediments dominates over manganese near the redox boundary. The majority of the manganese oxidation therefore occurs in the surficial, bioturbated sediments, and as a result, manganese-rich oxic sediments are formed. In contrast, in sediments with a deeper redox boundary (>10 cm), manganese oxidation near the

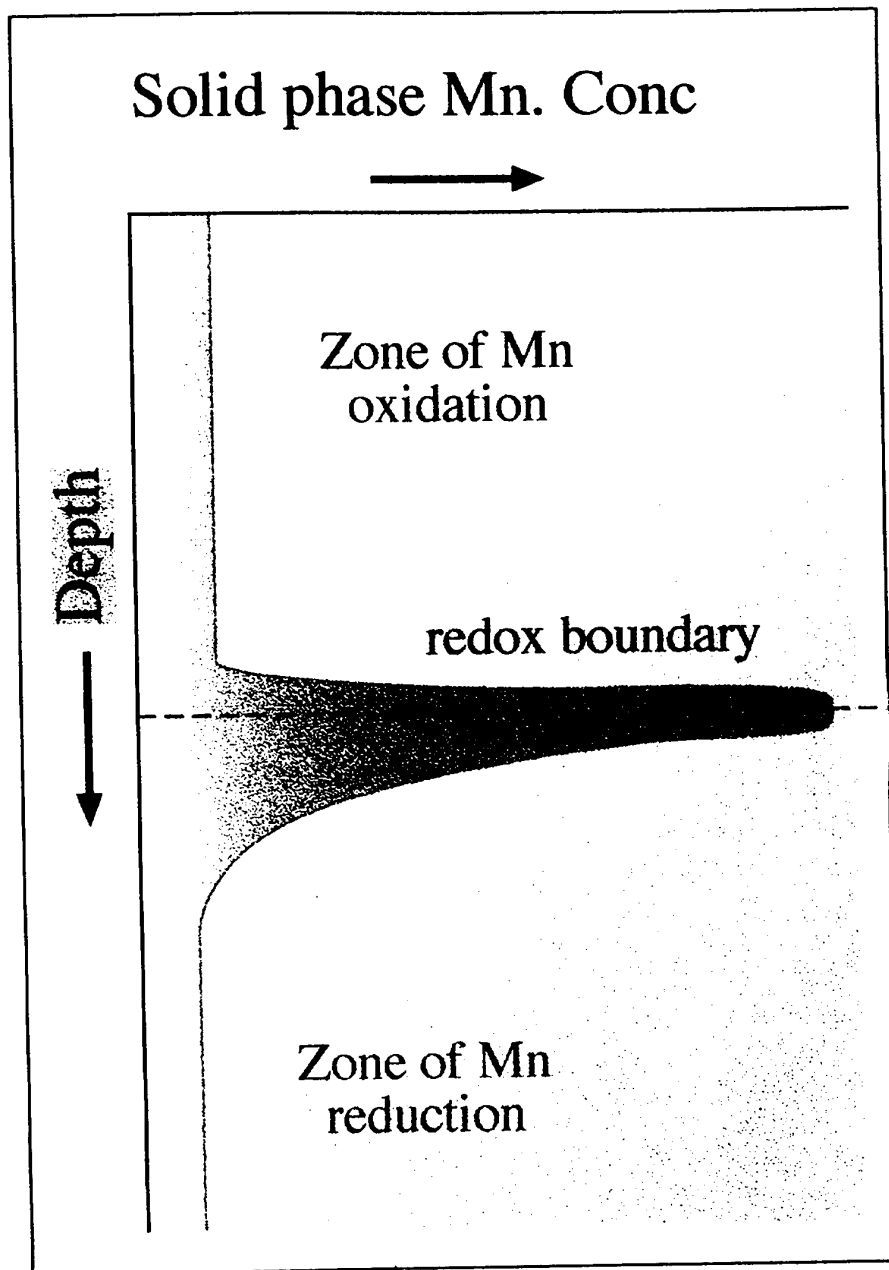
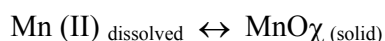


Fig. 1.2. The effects on solid phase manganese profiles due to changes in the depth of the redox boundary between the zones of manganese oxidation and reduction (Burdige, 1993).

sediment redox boundary dominates over pore-water manganese diffusion into the overlying oxic sediments.

The behaviour of manganese and iron, in both sea water and sediments has given rise to characteristic changes in dissolution, migration and precipitation of iron and manganese phases under conditions of low Eh and pH. The reduction of iron and manganese at depth in a sediment can be discerned by marked colour changes; i.e. brown (oxidizing conditions) and grey (reducing conditions). There is an inverse relationship between the thickness of the oxidizing layer in hemipelagic and pelagic sediments and the amounts of metabolizable OM contained in the sediments, which is also controlled to a considerable extent by the total sediment accumulation rate (Price and Calvert, 1970). When the sediments are deposited under oxic conditions, oxic diagenesis is initiated due to the degradation of OM, releasing metals which can be added to the particulate phase, either as adsorbed ions or as diagenetic/authigenic components of Mn-Fe oxides/hydroxides (Calvert, 1976; Chester, 1990).

The early diagenetic reactions of Mn during interstitial water/solid phase changes can be represented as



Where χ is greater than one and less than two.

The cycling of Mn in sediments can be illustrated by the model (Fig.1.3) proposed by Burdige and Gieskes (1983).

Oxidized Zone (Zone 1) : Dissolved Mn^{2+} is essentially at zero concentration in this zone, as any dissolved Mn that diffuses across the redox boundary is entirely

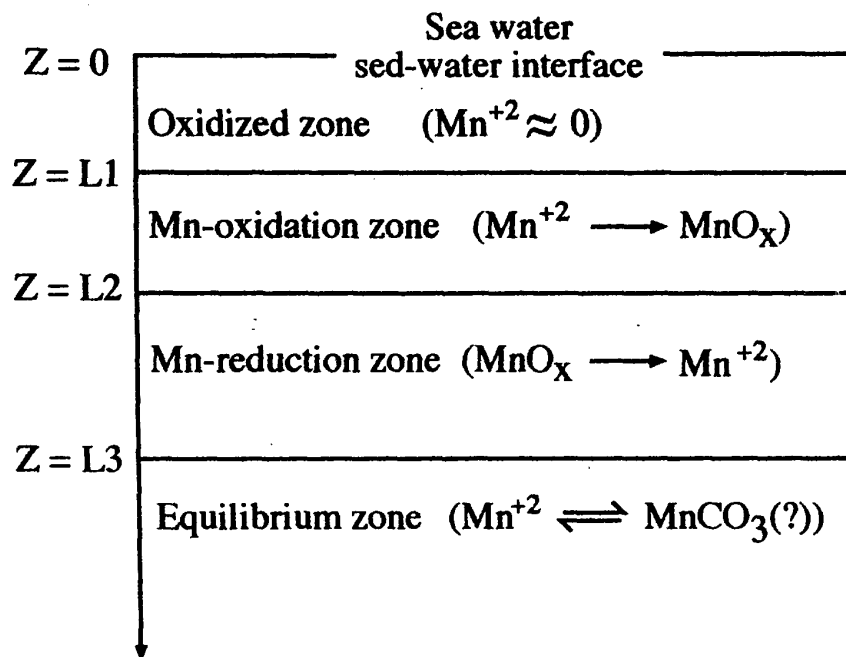


Fig. 1.3. Manganese diagenesis in marine sediments represents the sequence of zonation (Burdige & Gieskes, 1983).

consumed by oxidation before it reaches this zone. The first generation, or primary, Mn hydrous oxides are deposited in this zone, but are reduced by diagenetic reactions until they pass below the redox boundary.

Manganese Oxidation Zone (Zone 2): The concentration of dissolved Mn (Mn^{2+}_d) increases with depth in this zone and the profile is concave upward, i.e. it shows 'negative curvature'. The Mn^{2+}_d is oxidized and produces the hydrous oxide MnO_x . The product shows an increase in the concentration of Mn in the solid phase (Fig. 1.2).

Redox boundary (Zones 2 and 3): Zones 2 and 3 are separated by a redox boundary. This is the depth in the sediment at which dissolved Mn^{2+} is favoured over solid manganese oxide phases. There is a change of colour from brown (oxic) to grey/green (sub-oxic) in the sediments.

Equilibrium Zone (Zone 4): The dissolved Mn reaches a maximum and may decrease with depth. It is assumed that equilibrium with carbonate controls the concentration of dissolved Mn^{2+} at this zone.

The entire system can be described as follows. Manganese oxides in the surface sediments are buried as sediment accumulates. If organic carbon is also buried the diagenetic sequence will carry on at depth, and below the redox boundary, the oxides will be destroyed and Mn^{2+} is released in to the interstitial waters. The enhanced concentration of Mn^{2+} imposes a concentration gradient which leads to upward migration of Mn^{2+} and reprecipitation as hydrous Mn(IV) oxides in the presence of dissolved oxygen in the manganese oxidation zone. Hence, the hydrous manganese oxides (second generation) are produced as a result of diagenetic reaction, thus setting up the Mn re-cycling trap. The

theoretical interstitial water and solid phase manganese concentration profiles in the sequence are illustrated in Fig. 1.3.

1.5.2. Iron

Iron (Fe) is the fourth most abundant element present in the rocks of the Earth's crust, but is a relatively minor component in aquatic systems because of its relative insolubility in water. Iron exists in two oxidation states, ferrous (II) and ferric (III). Most magmatic rocks contain Fe in bound silicates in the divalent (reduced) state. Fe is released during the protolysis and oxidation of the rock. The liberated Fe (II) may be oxidized immediately if O₂ is present or, if not, as in deeper parts of the soil profile, it may migrate until reaching an oxygenated zone.

Fe (III)-(hydr)oxides are some of the most abundant soil minerals, and are a primary source of Fe, which is an important nutrient for the microorganisms and plants that inhabit the soil and marine environments (Lindsay, 1991). The important property of Fe is that it is found as very insoluble oxides in the most aerobic, natural environments. The sedimentary iron oxide mineral phases include goethite (α -FeOOH), ferrihydrite ($5 \text{ Fe}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$), akageneite (β -FeOOH), and lepidocrocite (γ -FeOOH) (Burns and Burns, 1977, 1981; Murray, 1979). The most common iron oxide mineral that is present in marine and freshwater sediments is magnetite (Fe₃O₄), a magnetic phase containing both Fe²⁺ and Fe³⁺; magnetite is found in marine sediments as a detrital component that is derived from the weathering of continental rocks, or from submarine (hydrothermal) volcanism (Murray, 1979).

Ferrous iron is less soluble than ferric iron and forms insoluble phases such as: siderite, FeCO_3 ; Pyrite, FeS_2 ; iron monosulphides, FeS ; vivianite, $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ (Emerson and Widmer, 1978; Berner, 1980, 1984; Postma, 1982). The reduction of iron oxides by sulfide has important implications in the formation of sedimentary pyrite and plays an important role in the global sulfur cycle (e.g. Berner, 1982, 1984; Garrels and Lerman, 1984).

Fe (III) reduction is an important processes for the degradation of naturally occurring OM in aquatic sediments, as well as for organic contaminants in polluted aquifers (Lovely, 1991, 1994). Indeed, iron reducing organisms can oxidize a wide range of aromatic organic compounds (Lovely, 1991). A major factor limiting the rate of microbial oxidation of organic matter coupled to Fe(III) reduction appears to be the ability of Fe(III) reducers to access the insoluble Fe(III)-oxides that serve as the principal source of microbially reducible Fe(III) in soils and sediments (Lovely, 1991; 1994). Numerous studies have confirmed that the reduction of Fe(III) oxides takes place via the direct interaction of Fe(III) reducing microorganisms (Munch and Ottow, 1983; Lovely, 1991).

Microbial manganese and iron reduction coupled to OM oxidation requires direct contact of the bacteria with the oxide surface (Tugel et al. 1986; Arnold et al. 1988; Ghirso, 1988; Myers and Nealson, 1988). Lab studies suggest that the rates of microbial manganese and iron reduction are a function of the mineralogy and/or specific surface area, of the oxides undergoing reductive dissolution (Lovley and Phillips, 1987, 1988; Burdige et al. 1992), with amorphous oxides generally showing greater reactivity than more highly crystalline forms.

The $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox boundary generally occurs below the manganese redox boundary in sediments (Thomson et al. 1995), often coinciding with a

brown to green colour transition in non-sulfidic (e.g. pelagic) sediments (Lyle, 1983). This colour change is reversible, and is apparently associated with the oxidation and reduction of iron in smectite clays, rather than the reductive dissolution of sedimentary iron oxides.

1.5.3. Copper

Copper is transported by organic carriers from the surface waters, but it is also scavenged in deep waters; however, it is regarded as a ‘nutrient-type’ element due to its depletion in surface waters (Bruland, 1980; Callender and Bowser, 1980; Whitfield and Turner, 1987; Chester, 1988). Under oxidizing conditions at the sediment-water interface most of the organic carrier phase of copper is destroyed, releasing Cu into the solution. Some of this copper migrates downward and is incorporated into the sediment, but most of it is recycled back into the water-column (Klinkhammer et al. 1986). However, under reducing conditions, relatively large amounts of organic carriers can be incorporated in the sediment, thus retaining some of their associated copper. A large percentage of total copper (ΣCu) reaching the sediment surface from the overlying water is associated with OM in the biogenic carriers which drive the oceanic carbon flux. Studies of the dissolved (interstitial water) and solid phase (sediment) distribution of copper have revealed the following general sequence of diagenesis of the element (Klinkhammer et al. 1982; Sawlan and Murray, 1983; Pedersen et al. 1986).

a) During oxic diagenesis, organic carriers are destroyed at, or near, the sediment surface, and the copper associated with them undergoes a rapid release. The

shapes of interstitial water profiles for oxic sediments (Klinkhammer et al. 1982) exhibit concentration gradients which occur due to both upward and downward diffusion of the released copper.

b) The upward diffusing copper mostly escapes into the overlying sea water following the destruction of the labile OM, and leads to an ocean-wide out-of-sediment copper flux (see e.g. Boyle et al. 1977). More than 90% of the copper flux to the sea floor is returned to sea water via diagenetic processes (Callender and Bowser, 1980; Klinkhammer et al. 1982). However, Klinkhammer et al. (1982) provided data which suggested that the amount of copper released in this manner at the sediment/water interface is very much larger than would be predicted from the decomposition of organic matter originating from plankton, and they concluded that the migration of dissolved copper from oxic marine sediments into the overlying sea water cannot be maintained by the release of the element from accumulating sediments. They suggested, rather, that the dissolved copper interstitial water profiles are sustained by scavenging of the element from the lower water column, and recycling across the interface, following the release of the element from a very thin, copper-enriched, 'scavenged' layer at the surface. The authors estimated that this layer should contain $\sim 2500 - \sim 5000 \mu\text{g g}^{-1}$ Cu, and subsequently Balistrietri and Murray (1984) collected interfacial particulate matter by submersible in the Pacific which contained $\sim 3000 \mu\text{g g}^{-1}$ Cu. This thin enriched copper layer probably exists in the so-called 'fluff' at the sediment surface.

c) The downward diffusing copper, which makes up only $\sim 10\%$ of that released from the labile organic carriers at the sediment-water interface, is taken up by the sediment and consumed by solid phases, which may include manganese oxides

(see e.g. Pedersen et al. 1986) in the form of ‘first generation’ (oxic) diagenetic copper.

d) During sub-oxic diagenesis at depth in the sediment, the ‘first generation’ copper, which has been scavenged at a higher level, may be released back into the interstitial waters, and may migrate either upwards or downwards (see e.g. Pedersen et al. 1986) as a result of the removal of dissolved copper by solid phases, such as manganese oxides as ‘secondary generation’ (sub-oxic) diagenetic copper.

e) It is apparent, therefore, that although the labile organic carriers are important in the down-column transport of copper, diagenetic release and bottom water scavenging reactions are involved in maintaining the diffusion of the element into sea water. However, the initial step in the overall process is the release of copper from the labile organic carriers. The preservation/destruction of the copper organic carrier phases in oceanic sediments is dependent on complex diagenetic processes which vary with the environment of deposition.

Chester et al. (1988) carried out a study of the solid state speciation of copper in surface water particulates and sediments from the Atlantic Ocean. They reported that ~50% of the ΣCu in the surface water particulates is held in organic associations. The preservation of this organically-bound copper in the underlying sediments could be related to the environment of deposition. i) The preservation of organically-bound Cu is highest in diagenetically-active hemi-pelagic sediments deposited in marginal regions, which have a relatively thin surface oxic layer. In these regions, the enhanced down-column carbon flux resulting from primary production in the overlying surface waters results in the burial of OM in the sediments which are deposited at relatively fast rates. Although some

of this OM is subsequently destroyed via the utilization of secondary oxidants, ~20% of the ΣCu is preserved in an organic-association. ii) The preservation of organically-bound Cu is lowest in the less diagenetically-active pelagic sediments deposited in open-ocean regions. Here, most of the down-column transported OM is destroyed at, or near, the sediment surface, and $<\sim 5\%$ of the ΣCu is preserved in an organic association. It may be concluded, therefore, that the amount of organically-associated Cu that is preserved in Atlantic deep-sea sediments mimics primary production in the overlying waters. However, this general relationship can be perturbed in open-ocean regions by turbidite deposits in abyssal plain regions. These turbidites originate on shelf regions and can bring relatively large amounts of OM, and “organically-associated” Cu, to the mid-ocean environment. These turbidites can, however, have their OM subsequently degraded by downward migrating diagenetic fronts (see i.e. Wilson et al. 1985).

1.6. Organic Matter Diagenesis

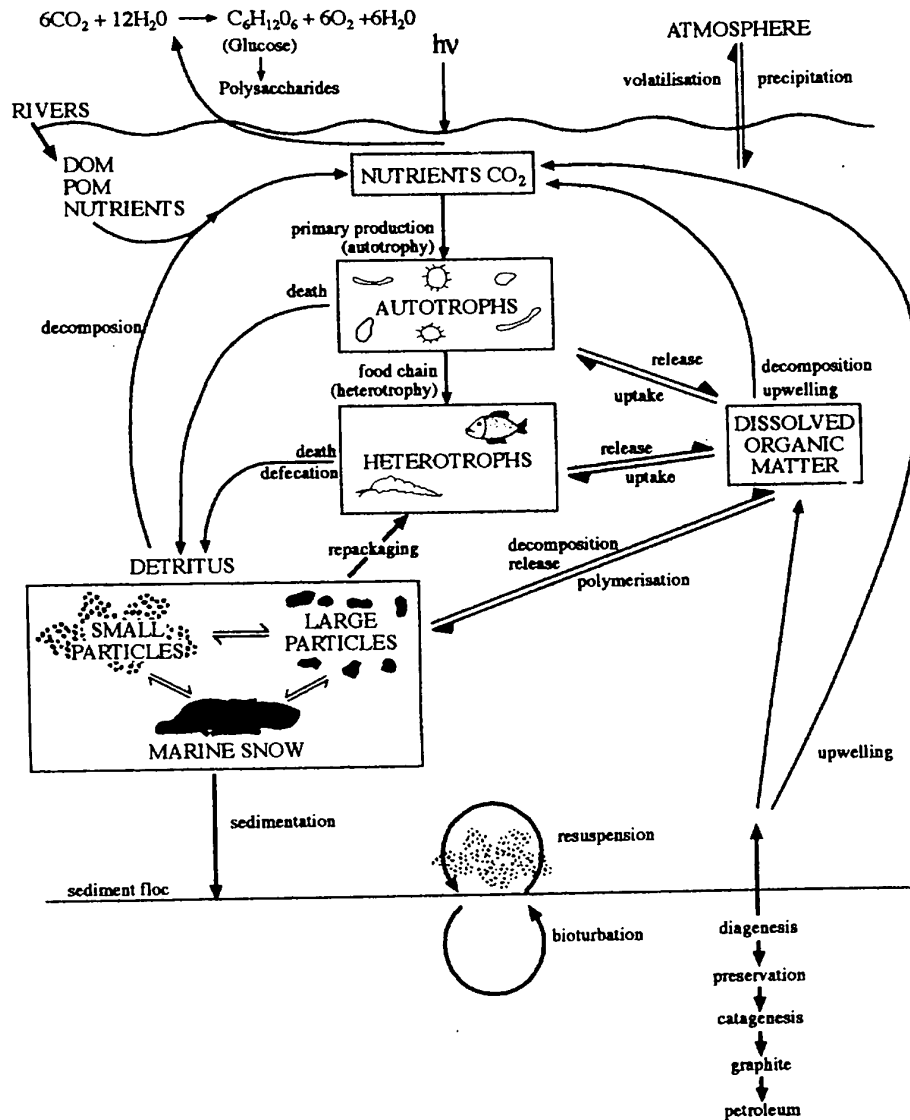


Fig.1.4. Organic matter cycling in the ocean.
(after Lee and Wakeham, 1989).

1.6.1. Production of Organic Matter

Photosynthesis is the basic process in the mass production of organic matter (OM). During photosynthesis, OM is produced in the form of glucose by reduction of CO₂, with release of oxygen (Fig.1.4). In the oceans, the photosynthetic organisms are principally unicellular phytoplankton (Killops and Killops, 1993). These autotrophic organisms can biosynthesize polysaccharides, such as cellulose and starch and all other necessary constituents from glucose.

1.6.2. Composition of Organic Matter

Organic matter is composed of labile and refractory compounds which are principally composed of carbon, hydrogen, oxygen, nitrogen, and sulphur. OM is the source of electrons that drives most biologically mediated redox reactions. Three important biochemical constituents of OM include carbohydrates, proteins and fatty acids and these have been used to estimate the labile portion of OM (Daumas *et al.* 1983; Fichez, 1991; Danovaro *et al.* 1993). The characterization of sedimentary OM at the molecular or compound levels (*i.e.* lipids, carbohydrates and amino acids) provides information on the diagenetic history, and sources of OM in the sedimentary deposits (Engel and Macko, 1993).

Concentrations of organic carbon (TOC) are generally low in open ocean sediments, often less than 0.2% TOC in normal deep-sea environments (McIver, 1975). However, in sediments deposited in upwelling areas of high productivity, TOC contents are often higher (>1%); in such organic rich environments, for example in rapidly depositing coastal sediments, the average composition of OM

would typically be: hydrolysable carbohydrates (5%), hydrolysable amino acids (10-15%), lipids (<5%), lignin (<3%) and volatile fatty acids (<1%). However, more than 70% sedimentary OM cannot be readily identified and is included in the operationally defined OM fractions fulvic acid, humic acid, and humin (Henrichs, 1992). These become more important with increasing sediment age, so that the chemical and microbially mediated reactions of the OM results in the formation of “geopolymers” and ultimately kerogen (Nissenbaum and Schallinger, 1974; Welte, 1974).

1.6.3. Sources of Organic Matter

Organic matter in oceanic sediments can be either of marine (autochthonous) or terrigenous (allochthonous) origin. Terrigenous OM is delivered to the ocean environment by both aeolian and river transport, whilst marine OM is mainly derived from photosynthetic primary production in the surface waters. The latter is usually the major source of organic carbon to marine sediments. Autochthonous OM is mostly recycled in the upper few hundred metres of the water column and only a small fraction of the particulate OM reaching the seafloor is preserved in the sediments (Fig.1.4).

1.6.4. Significance of the study of OM

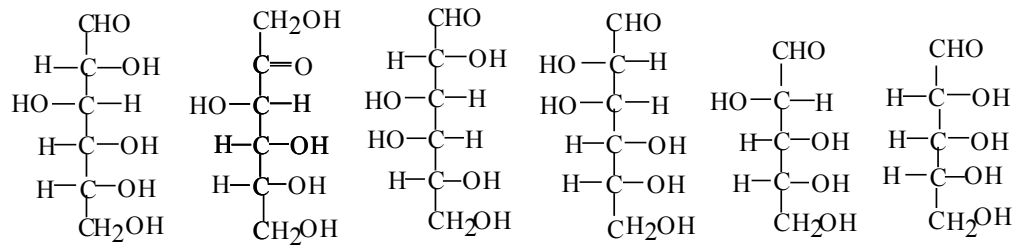
The study of the biogeochemistry of organic compounds in sediments is important in the understanding of the degradation and recycling of organic matter (OM) by benthic micro - and macroorganisms in marine sediments. The processes involved can be quantified by examination of the concentrations of the major organic chemicals (e.g. Henrichs, 1993; Smith et al. 1992). The extent of degradation of OM in recent sediments is directly related to the amount and nature of the inputs of particulate material at the sediment-water interface (Emerson et al. 1985; Mann, 1986). Most studies deal with the concentrations of one or other compound class, and few have attempted to identify all of the OM in a sedimentary sequence. However, there have been some detailed studies which have provided information on the mass balance and diagenesis of major biochemicals in organic rich sediments (Reimers and Suess, 1983; Henrichs et al. 1984; McCaffrey et al. 1990; Seifert et al. 1990; Patience et al. 1990, ten Haven et al. 1992; Lewis and Rowland, 1993).

Relevant aspects of organic geochemistry, such as biochemical fluxes (e.g. amino acid and carbohydrates; Ittekkot et al. 1984 a,b; Klok et al. 1984 a,b,c; Cowie, 1990), distribution of specific lipid classes (Van Vleet, 1979; Volkman et al. 1987), elemental composition (Müller, 1977; Verardo et al. 1990) and kerogen (Durand, 1984) have been reviewed recently (Engel and Macko, 1993). It is beyond the scope of this thesis to review these in detail, however, in the following sections the diagenetic fate of carbohydrates and proteins will be briefly discussed.

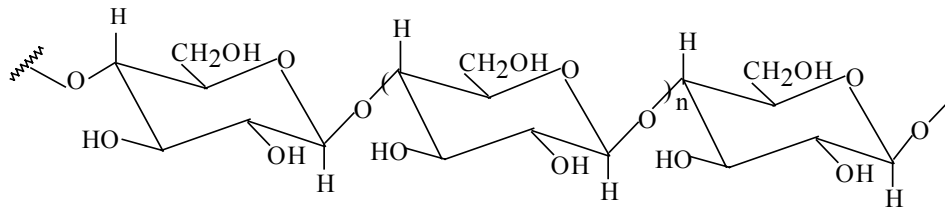
1.6.5. Carbohydrates

Carbohydrates contain carbon, hydrogen and oxygen in the ratio of 1:2:1, with the general formula $C_n(H_2O)_n$. Certain carbohydrates also contain nitrogen or sulphur. They can be defined as polyhydroxylated compounds, which include aldehydic or ketonic groups, or yield such groups on hydrolysis. The principal building blocks of carbohydrate chemistry are the monosaccharides which contain from three to eight carbon atoms. Carbohydrates are classified into three main groups as monosaccharides, oligosaccharides and polysaccharides (Fig. 1.5). **Monosaccharides** are simple sugars and classed as aldoses and ketoses, which contain aldehyde and keto groups respectively. The number of carbon atoms in the molecules is indicated by the name i.e. trioses, tetroses, pentoses, hexoses and heptoses. For example, an aldohexose is a simple sugar containing six-carbon atoms and an aldehyde group (e.g. glucose; Fig.1.5); a ketohexose is a six-carbon monosaccharide containing a keto group (e.g. fructose; Fig.1.5). Most naturally occurring monosaccharides are pentoses or hexoses. **Oligosaccharides** are carbohydrates which yield two to ten monosaccharides units on hydrolysis. Depending on the number of constituent monosaccharide units, the **oligosaccharides** are called **disaccharides**, **trisaccharides** etc. The most important disaccharides are sucrose, lactose and maltose. **Polysaccharides** are defined as high-molecular weight carbohydrates containing many (tens, hundreds or thousands) of monomeric units connected to one another by a covalent bond referred to as glucosidic bond. These carbohydrates, yield more than ten molecules of monosaccharides on hydrolysis. The most important polysaccharides are the

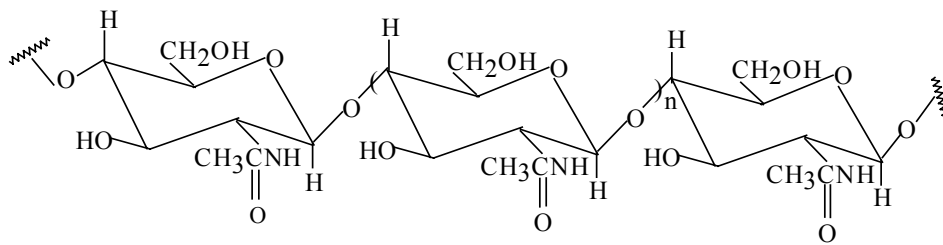
starches, the glycogens, the dextrans obtained from starch and glycogen, the celluloses and chitin.



Glucose Fructose Galactose Mannose Arabinose Ribose



Cellulose



Chitin

Fig.1.5. Structures of carbohydrates and sugars.

1.6.5.1. Carbohydrates in the marine environment

Carbohydrates in the marine environment derive from both marine and terrestrial sources. The three major inputs to coastal or estuarine environments are land plants, macroalgae and phytoplankton. They occur as free (as free sugars such as monosaccharides and oligosaccharides) or combined forms. Combined carbohydrates may be either polysaccharides or low-molecular weight sugars which are tightly bound in some manner to various sedimentary materials.

Typically, carbohydrates comprise 2-4% dry wt. of marine zooplankton, 20-70% dry wt. of marine algae, 10-30% of particulate organic carbon (POC), and up to 20% of DOC in seawater (Burney et al. 1979; Harvey, 1983; Romankevich, 1984). Higher plants are mostly built of cellulose (~40%) and secondly of hemicellulose (xylans in angiosperms, mannans in gymnosperms).

The carbohydrates are major constituents of phytoplankton (Parsons et al. 1961; Hecky et al. 1973; Haug and Mykkestad, 1976) and of their extracellular products (Helleburst, 1974). In plankton-derived organics they are composed of rhamnose, fucose, ribose, arabinose, xylose, mannose, galactose and glucose (Handa and Yanagi, 1969; Modzelski et al. 1971). Carbohydrates in phytoplankton can form the three major groups in relation to structural and biochemical functions (Tanoue and Handa, 1987).

1) Glucose which is important in storage polysaccharides of phytoplankton; their concentration increases in phytoplankton with increasing age (Mykkestad, 1977).

2) Galactose is a major constituent of diatom cell walls (Hecky et al. 1973).

3) Galactose, fucose and rhamnose are important in extracellular polysaccharides, together with lesser amounts of xylose, mannose and galactose.

The cell wall polysaccharides are the important source of carbohydrates in the deep-water particulates and bottom sediments (Tanoue and Handa, 1987).

The biogeochemistry of carbohydrates in the marine environment has been the subject of several reviews (Mopper, 1973; Mopper et al. 1980; Romankevich, 1984; Thurman, 1985). Studies of lacustrine (e.g. Liu, 1976), estuarine (Hadzija et al. 1985) and marine sediments (Artem'yev, 1969; Tanoue and Handa, 1987) have also been reported in the literature. Furthermore, the sources of carbohydrates in the sediments of a coastal marine bay have been elucidated (Cowie and Hedges, 1984b, Hedges et al. 1988). Carbohydrates are often associated with proteins (in peptidoglycans), lipids (in glyco-lipids and lipo polysaccharides), phenolic substances (lignin) and even with minerals (silicates, phosphates and carbonates).

Biopolymeric carbohydrates are degraded by microbial activity into individual sugars, some of which are utilized for nutrition. The residues which are not utilized by microbes, as they are resistant towards biological decay, undergo polycondensation and polymerisation to form brown compounds similar to fulvic and humic acids. These can potentially become part of the insoluble OM in the sediments (Klok et al. 1984b). These processes take place mostly at or near the water-sediment interface (Tissot and Welte, 1984). Carbohydrates are thus considered to be important precursors for the formation of humic acids and kerogens etc., which are presently widely distributed and abundant in sediments (Fig.1.6). The presence of high amounts carbohydrates as constituents of humic substances has been reported for both marine and terrestrial sources (Sweet and Predue, 1982; Yamoka, 1983a,b; Sakugawa and Handa, 1985; Rashid, 1985;

Kalinowski and Blondeau, 1988). The monosaccharides in humic and fulvic acids in the sediment consist of rhamnose, fucose, arabinose, xylose, mannose, galactose, and glucose (Yamoka, 1983 a, b).

The concentrations of carbohydrates in surface sediments (0-5 cm) from the Pacific, Atlantic and Indian Oceans, vary from 66 to 21,333 mg/g which is more than 300 fold variation. Maximum concentrations are characteristically observed in the shallow water zones of high biological productivity, whilst minimum levels are found in pelagic deposits (Romankevich, 1984). A direct relationship, with high correlation coefficient has been established between the carbohydrate and total organic carbon contents of various sediments from the Pacific and Atlantic Oceans. However, this is less significant in the sediments of the continental margin, which are subjected to regional differences in the OM composition, and is absent in pelagic areas, where the concentrations of carbohydrates and organic carbon are both very low. Carbohydrate concentrations tend to decrease with increasing water depth and distance from shore, presumably because of the longer residence times of organic particles and their intensive degradation during descent through the water column at the continental margins (Steinberg et al. 1987).

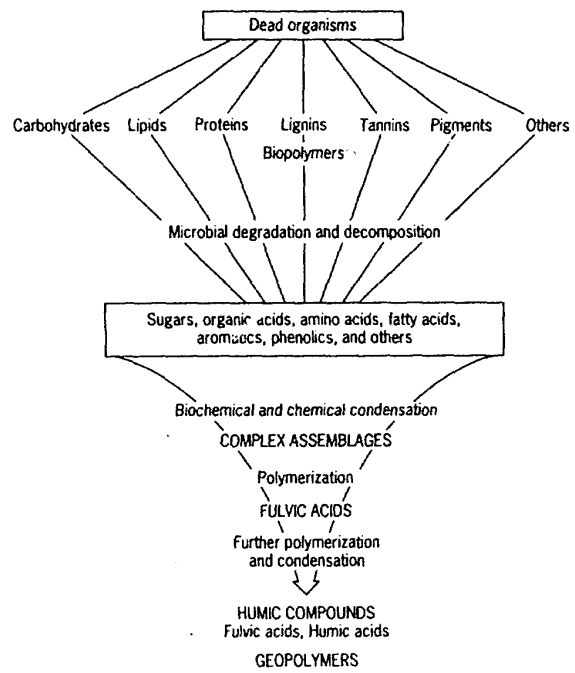
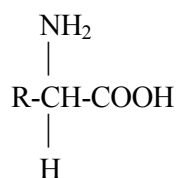


Fig.1.6. Processes of degradation of organic compounds (S. M. Libes, 1992).

1.6.6. Proteins

The name 'protein' is derived from the Greek *proteis*, which means first. Proteins are polyamide bio-polymers resulting from the condensation α -amino carboxylic acids. All amino acids contain carbon, hydrogen, oxygen, nitrogen and two important functional groups, a carboxylic acid group (-COOH) and an amino group (-NH₂). The general formula of these acids is represented by



where 'R' denotes a variety of groups .

Two of the twenty common amino acids found in cells also contain sulphur atoms (e.g. Fig.1.7). Proteins are composed of hundreds or thousands of amino acids as monomeric building units linked by peptide bonds. Their hydrolysis, therefore, results in the cleavage of these bonds, ultimately leading to the formation of free amino acids. There are twenty two different kinds that are usually classified as aliphatic, aromatic and heterocyclic compounds.

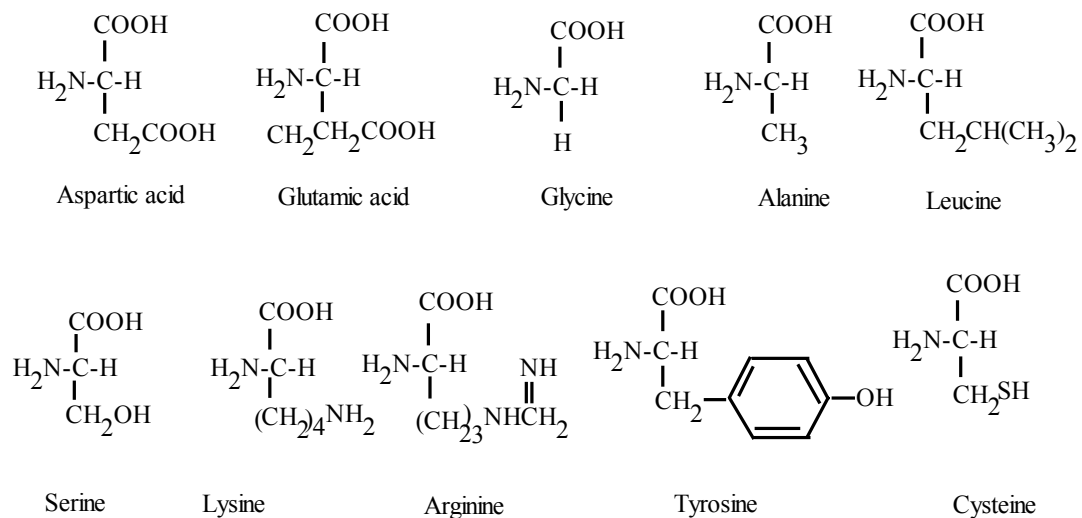


Fig. 1.7. Structures of amino acids.

The average elemental composition of proteins is carbon (50-55%), hydrogen (6-8%), oxygen (20-23%), nitrogen (15-18%) and sulphur (0-4%). Proteins are the major cellular constituents of phytoplankton, and 85% of phytoplankton nitrogen is in this form (e.g. Billen, 1984). The significance of the study of proteins in the marine environment has increased as the importance of these biomolecules in cellular function, trophic transfer, and biogeochemical cycling have been recognized. Proteins may also represent an important source of carbon and nitrogen in marine systems.

1.6.6.1. Proteins in the marine environment

A number of studies concerned with amino acids and proteins have reported that these are the major constituents of total nitrogen in recent marine sediments (Henrichs and Farrington, 1987; Burdige and Martens, 1988). Protein concentrations account for up to 95% of total organic nitrogen in a coastal marine surface sediments (Mayer and Rice, 1992) and amino acids account for ~70% of total nitrogen in the surface sediments of Peru upwelling area (Seifert *et al.* 1990). Amino acids play significant role in a number of chemical and biochemical processes occurring in the water column and sediments; their compositions change markedly during particle transport, sedimentation and diagenesis. For example, nearly 100% of the nitrogen in sediment trap materials is present as amino acids (Biggs *et al.* 1988, 1989) but as little as ~2-12% of the nitrogen in upper sediments are characterized as amino acids (Rosenfeld, 1979; Mayer *et al.* 1988). Nevertheless, even though amino acid concentrations are rapidly attenuated with increasing depth in the water column (Wakeham *et al.* 1984), they are present in sediment traps and sediments at abyssal depths (Macko, 1992), thus revealing the source of labile organic carbon and nitrogen to abyssal benthic fauna.

Labile nitrogenous compounds are an important source of nutrition in marine sediments which are zones for heterotrophic activity. They have been characterized in the literature primarily as total organic nitrogen (TN) or, in some cases, as total acid-hydrolyzable amino-acids (THAA). These two parameters show no detectable changes in the composition during downcore diagenesis (*i.e.* Henrichs and Farrington, 1987; Burdige and Martens, 1988), although sediments may include a

considerable amount of refractory material that is not susceptible to heterotrophic processes during early diagenesis.

Furthermore, the high molar percentage of acidic amino acids in phytoplankton (Degens and Mopper, 1975; Wakeham *et al.* 1984b), decreases due to degradation by bacteria as phytoplankton sink through the water column. Hence, acidic amino acids decrease in relative concentration compared to the neutral amino acid fraction with increasing particle age (Steinberg *et al.* 1987).

THAA compositions vary only slightly with depth (Henrichs *et al.* 1984; Rosenfeld, 1979), which may reflect the uniform composition of proteinaceous material or imply similar rates of decomposition for individual amino acids (Henrichs *et al.* 1984). The compositions of THAA in deep-sea sediments show high levels of non-protein amino acids, β -alanine and γ -aminobutyric acid and the basic amino acid histidine (Wakeham *et al.* 1984; Whelan, 1977). THAA compositions having higher concentrations of glycine than aspartic acid, glutamic acid, alanine and serine have been recorded in near-shore/continental margin sediments, but with low concentrations of non-protein amino acids such as, β -alanine, γ -aminobutyric acid and hydroxyproline (Henrichs and Farrington, 1987; Henrichs *et al.* 1984; Maita *et al.* 1982).

The acidic (*i.e.* aspartic acid and glutamic acid) and hydroxy-amino acids are generally more easily decomposed than the basic amino acids in deep-sea sediments, the latter becoming relatively more abundant with increasing sediment depth (Rosenfeld, 1979; Seifert and Michaelis, 1991; Horsfall and Wolff, 1997); The mechanism proposed for the destruction of amino acids is the decarboxylation of aspartic and glutamic acid to form the non-protein amino acids, β -alanine and γ -aminobutyric acid (Rosenfeld, 1979). Polypeptide chains are prone to more rapid

degradation at acidic (or aromatic) amino acid sites by deamination (Maita et al. 1982). Additionally, basic amino acids may be preferentially preserved, since they are also more strongly sorbed onto OM and clay minerals than acidic and neutral amino acids (Rosenfeld, 1979; Stevenson and Cheng, 1970).

1.7. This Study

Organic matter (OM) in marine sediments consists of detritus derived from terrestrial (allochthonous) and aquatic (autochthonous) biota, which is modified by microbial activity both before and after deposition. The organic constituents of sediments in the marine environment play a significant role in biochemical and geochemical processes; for example, their reactions control the diagenetic behaviour of a number of trace metals and their cycling and subsequent release to overlying waters. Manganese and iron, when present in the form of solid phase oxides and oxyhydroxides are important secondary oxidants in the degradation of sedimentary OM under sub-oxic conditions (see Section 1.4). These reactions have been investigated thoroughly in marine sediments, but their relationship with the diagenesis of OM has not been directly established. Hence, a study of the diagenesis of OM and trace metals in sediments from the Indian Ocean (Arabian Sea) has been undertaken in order to gain an understanding of the relationship between the biogeochemistry of OM and diagenetic active trace metals. To the best of the knowledge of this author, studies dealing with trace metal speciation and its association with organic matter in Arabian Sea sediments are sparse. Few studies exist on organic-rich sediments and attempts to assess the manner in which the degradation of individual organic components affects the solid state speciation of trace metals in the sediments of the NW Indian Ocean (Arabian Sea). In particular, down-core variations in the speciation signatures of Mn, Fe and Cu and changes in the nature of the OM to establish the degree of ‘diagenetic coupling’ between them. This might ultimately provide information on palaeoceanic conditions and changes in primary productivity.

The overall objectives of the work were, therefore:

- 1) To assess the level of the diagenetic alteration of OM in the sediments in order to establish the extent to which they act as traps for 'old' (refractory) and/or 'new' (marine-derived) labile OM.
- 2) To relate the OM-mediated diagenetic processes to changes in the solid state speciation signatures of Mn, Fe and Cu, and to establish the degree to which the changes control the cycling of the metals.
- 3) To assess the extent to which the sediments act as sources or sinks for the trace metals in the land/sea transport cycle.

In order to test the 'geochemical consistency' of the sequential leaching data, samples were initially chosen from abyssal sediments; the first phase of the investigation was carried out along with OM analyses on two 'diagenetically-active' sediment cores from the Arabian Sea (Chapter 4). In the second phase, similar analyses were applied to three replicate sediment cores from the most intense part of the OMZ (Chapter 5).

The unique characteristics of the Arabian Sea are reviewed in Chapter 2, whilst Materials and chosen methods are described in Chapter 3.