# REVIEW PAPER

# Comparative organic geochemistries of soils and marine sediments

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**Abstract**—Striking similarities and sharp contrasts exist between the geochemistries of organic matter in surface soils and marine sediments. The contrasts result in part from physical differences in the two environments and their indigenous biota. Vascular plants predominate on land, where soils are deeply leached by percolating water and receive organic matter from falling debris and penetrating roots. The large size of vascular plants, and their high concentrations of carbon-rich biomacromolecules such as cellulose, lignin and tannin, necessitate recycling by aggressive consortia of microorganisms, including fungi armed with $O_2$-requiring oxidative enzymes. In the ocean, nitrogen-rich microorganisms produce and recycle most organic matter in the water column, from which degraded particles rain onto the underlying sea floor. Water saturation restricts $O_2$ penetration into sediments accumulating along most continental margins to less than several centimeters, below which biomacromolecules must be broken down hydrolytically with nitrate and sulfate as the primary electron acceptors.

In both soils and sediments, plant products are degraded extensively by microorganisms, leaving small organic remnants which are soluble in base and depleted in conventionally measurable biochemicals. Much of the surviving organic matter is intimately associated with mineral surfaces and enclosed within particle aggregates, and thus may be physically protected from microbial attack. Degradation under oxic conditions is severe both on land and within surface ocean deposits. As a result, even physically protected organic matter can slowly be mineralized, along with intrinsically resistant substrates such as lignin, pollen, kerogen and coal. The only long-term shelter from mineralization is within anoxic marine sediments which accumulate one mole of organic carbon for every 500–1000 fixed by photosynthetic organisms. The buried organic matter joins the geological cycle, surfacing again millions of years later as kerogen uplifted in continental rocks.

Chemists investigating organic matter in soils or sediments employ distinct strategies and experimental methods for disparate purposes. Soil studies focus primarily on bulk properties linked to complex system functions such as fertility and erosion. Investigations of sedimentary organic matter are more molecularly-based and directed toward interpretations of water column processes and paleorecords. With the pressing need for more efficient large-scale research, the time is ripe for increased interchange between chemists studying subaerial and subaqueous systems. Combination of methods (such as preparative particle sorting and solid-state NMR) for determining the forms and physical distributions of organic matter in soils, with highly sensitive tracer techniques being developed in the aquatic field is a particularly promising crossover area. The aim of this review is to facilitate such interactions between soil and sedimentary organic geochemists by a comparative evaluation of conditions, concepts and opportunities in both fields. © 1997 Published by Elsevier Science Ltd. All rights reserved

*Key words*—soil geochemistry, sediment, global cycles, NMR, biomarker, organic matter preservation, sorption, aggregates, analytical geochemistry

## INTRODUCTION

Soils and surface marine sediments incorporate two of the largest and most dynamic reservoirs of organic matter on earth (Siegenthaler and Sarmiento, 1993). In both environments, complex mixtures of degraded plant and animal remains are disseminated with mineral particles, water and living organisms. Soils, however, are transient, heterogeneous assemblages that occur uniquely at one of the most variable interfaces on earth and are subject to fluctuating redox conditions, leaching and erosion. Surface marine sediments accumulate under a blanket of water, are more homogeneous and closed, and eventually lapse into long-term anoxia. Large vascular plants, which predominate on land and contribute to soil organic matter by litterfall and direct root injection, are essentially absent from the ocean, where microorganisms with distinctly different biochemical compositions are the major producers and degraders of organic matter.

Although typically present at concentrations of ten weight percent or less, nonliving organic materials strongly affect the physical and chemical

Table 1. Books and articles on soil and sedimentary organic matter

| Title | Authors and year |
| --- | --- |
| **Soil Organic Matter Books** | |
| Soil Organic Matter | Kononova, 1966 |
| Organic Chemicals in the Soil Environment | Goring and Hamaker, 1972 |
| Soil Biochemistry, Volumes 1–8 | Paul et al., 1967–93 |
| Soil Organic Matter and its Role in Crop Production | Allison, 1973 |
| Soil Components (Vol. 1), Organic Components | Gieseking, 1975 |
| Soil Organic Matter | Schnitzer and Khan, 1978 |
| Nature and Origin of Carbohydrates in Soils | Cheshire, 1979 |
| Humus Chemistry, Genesis, Composition, Reactions | Stevenson, 1994 |
| Soil Organic Matter and Biological Activity | Vaughn and Malcolm, 1985 |
| Interactions of Soil Minerals with Natural Organics and Microbes | Huang and Schnitzer, 1986 |
| Soil Organic Matter | Tate, 1987 |
| Chemistry of Soil Organic Matter | Kumada, 1987 |
| Dynamics of Soil Organic Matter in Tropical Ecosystems | Coleman et al., 1989 |
| Soil Microbiology and Biochemistry | Paul and Clark, 1989 |
| Humic Substances in Soil and Crop Science | MacCarthy et al., 1990 |
| Advances in Soil Organic Matter Research | Wilson, 1991 |
| Evaluation of Soil Organic Matter Models | Powlson et al., 1996 |
| **Soil Organic Matter Review Articles** | |
| The retention of organic matter in soils | Oades, 1988 |
| An introduction to organic matter in mineral soils | Oades, 1989 |
| Soil organic matter — The next 75 years | Schnitzer, 1991 |
| Physical fractionation of soil and organic matter in primary particle size and density separates | Christensen, 1992 |
| Soil structure and biological activity | Ladd et al., 1996 |
| **Sedimentary Organic Matter Books** | |
| Organic Geochemistry | Eglinton and Murphy, 1969 |
| Marine Organic Chemistry | Duursma and Dawson, 1981 |
| Geochemistry of Organic Matter in the Ocean | Romankevich, 1984 |
| Geochemistry of Marine Humic Compounds | Rashid, 1985 |
| Biological Markers in the Sedimentary Record | Johns, 1986 |
| Organic Marine Geochemistry | Sohn, 1986 |
| Organic Matter | Whelan and Farrington, 1992 |
| Marine Organic Geochemistry: Review and Challenges for the Future | Farrington, 1992 |
| Biological Markers in Sediments and Petroleum | Moldowan et al., 1992 |
| Organic Geochemistry | Engel and Macko, 1993 |
| An Introduction to Organic Geochemistry | Killops and Killops, 1993 |
| The Biomarker Guide | Peters and Moldowan, 1993 |
| **Sedimentary Organic Matter Review Articles** | |
| The organic chemistry of marine sediments | Simoneit, 1978 |
| Organic geochemistry of particulate organic matter in the ocean: the role of particles in oceanic sedimentary cycles | Wakeham and Lee, 1989 |
| The early diagenesis of organic matter in marine sediments: Progress and Perplexity | Henrichs, 1992 |
| Processes that control storage of nonliving organic matter in aquatic environments | Reeburgh, 1995 |
| Sedimentary organic matter preservation: An assessment and speculative synthesis | Hedges and Keil, 1995 |
| **Crosscutting Books on Organic Matter** | |
| The Chemistry of Clay-Organic Reactions | Theng, 1974 |
| Formation and Properties of Clay-Polymer Complexes | Theng, 1979 |
| Aquatic and Terrestrial Humic Substances | Christman and Gjessing, 1981 |
| Organic Geochemistry of Natural Waters | Thurman, 1985 |
| Humic Substances in Soil, Sediment and Water | Aiken et al., 1985 |
| NMR Techniques and Application in Geochemistry and Soil Chemistry | Wilson, 1987 |
| Humic Substances and Their Role in the Environment | Frimmel and Christman, 1988 |
| Organic Acids in Aquatic Ecosystems | Perdue and Gjessing, 1990 |
| Environmental Organic Chemistry | Schwartzenbach et al., 1993 |
| Humic Substances in the Global Environment | Senesi and Miano, 1994 |
| The Role of Nonliving Organic Matter in the Earth's Carbon Cycle | Zepp and Sonntag, 1995 |

properties of the soils and sediments in which they occur, and hence the potential of these systems to host living organisms, record paleoenvironmental events, and store biologically-active elements. The quantities and compositions of organic matter in these deposits are not only critical to fertility and fossil fuel generation, but are also key considerations in global cycles and budgets. Not surprisingly, soil and sedimentary organic substances have been the subject of active scientific investigation for over 100 years. It is peculiar in light of these parallel environmental functions and the common bond of organic chemistry, that geochemists studying organic materials in soil and recent sediments continue to operate as two largely isolated guilds. Soil and sedimentary geochemists use disparate terminologies, embrace contrasting research styles, attend different scientific meetings, and support largely separate literatures. Continuing maturation of both fields, increasing emphasis on large-scale

systems, and the practical need for more efficient research, all provide impetus to geographically meld organic geochemical studies.

The two aims of this overview are (a) to integrate at a general level present knowledge on soil and sedimentary organic geochemistry and (b) to encourage increased understanding and interaction between scientists studying these contrasting environments. After a brief review of early developments in each field, the contrasting physical and chemical characteristics of soils and surface marine sediments and their characteristic biota will be discussed. This comparison will be limited to the upper meter of soils and continental margin sediments, the main repositories of actively cycling organic matter at the earth's surface. The often different methodologies employed to study organic substances in these two environments will be viewed in light of their contrasting biogeochemical settings, and the practical goals of scientists involved. Comparative distributions and reactions of organic matter in soils and sediments will then be highlighted. Finally, potentially useful parallels in current understandings of the organic geochemistries of terrestrial and marine systems will be discussed along with promising areas of potential overlap and cooperation. Although this overview is necessarily selective, numerous comprehensive texts and in-depth reviews of both soil and sedimentary organic matter are currently available (Table 1).

*Historical backgrounds*

The first studies of organic matter in the environment involved soils almost exclusively (Kononova, 1966; Stevenson, 1994). As early as the second half of the 18th century, it was recognized that soil organic matter is derived from decomposition of plants and animals and is beneficial to fertility. Humic geochemistry began over 200 years ago when Achard (1786) demonstrated that alkali solutions extract a brown substance from peats which upon acidification yields a precipitate now known as humic acid. In the next hundred years, humic acids were shown to be organic, acidic, and chemically similar to brown substances dissolved in rivers. During this time the role of humus in soil formation, the carbon cycle and nutrient availability to plants was recognized (Liebig, 1840). Following discovery of microorganisms by Pasteur, it became clear in the latter half of the 19th century that soil humus formation is predominantly a biological process. By the early 20th century, chemistry was sufficiently advanced that specific organic compounds in soil humus could be detected (e.g. Schreiner and Shorey, 1908). It soon became evident that soil organic matter is chemically complex and poor in recognizable biochemicals, characteristics that were hypothesized by some to result from spontaneous condensation of degradation intermediates from

vascular plants and microorganisms (Maillard, 1913; Waksman, 1936). Identification of structural features diagnostic of different biochemical precursors and formation pathways has been a continuing theme in soil organic matter research (Schnitzer and Khan, 1978; Senesi and Miano, 1994), strongly supported by application of developing analytical techniques such as cross-polarization, magic-angle spinning (CP/MAS) $^{13}$C NMR (Wilson, 1987; Preston, 1996).

Studies of sedimentary organic matter have a shorter history, much of which is traceable to the practical goal of identifying the origin of petroleum and marine depositional conditions under which it forms (Trask, 1932). Early research was primarily limited to determining total organic contents of surface marine sediments (Verigo, 1888). The generally recognized advent of the modern field was the discovery of chlorophyll-derived porphyrin pigments in petroleums and in "bitumen" extracted from ancient rocks by nonpolar solvents (Treibs, 1934). Investigations of humic substances in marine sediments followed, incorporating techniques and terminologies developed earlier for soils (Rashid, 1985). Research expanded greatly following World War II and by the late 1960s, the sedimentary distributions and reactions of many types of biochemicals (e.g. hydrocarbons, fatty acids, pigments, amino acids and carbohydrates) had been determined (Eglinton and Murphy, 1969). Emphasis later shifted toward studies of the environmental fates of petroleum-derived and synthetic organic chemicals (Goldberg, 1975). A major recent focus has been on the complementary use of biochemical compositions and bulk organic chemical properties to indicate paleooceanographic conditions and delineate global cycles (Macko and Engel, 1993). Throughout this development, lipid compounds, molecular-level tracers (biomarkers) of organic matter sources, and sedimentary records have been emphasized. This focus is traceable in part to the stability and high information content of lipids, as well as to a close association between oceanographers studying contemporary marine depositional environments and petroleum geochemists dealing with ancient counterparts.

*Organizations*

Three of the largest associations of organic geochemists are the International Humic Substances Society (IHSS), the European Association of Organic Geochemists (EAOG) and the Organic Geochemical Division of the Geochemical Society (OGD/GS). The IHSS currently lists about 350 geochemists, of whom roughly one-third are in organizations specializing in soil research and another fourth are based in aquatic or geologic research institutions. The IHSS was formed in 1981 and holds biannual meetings whose proceedings have been

Table 2. Journals carrying articles on soil and sedimentary organic matter

| Title | Organization or publisher | ISSN | Begun |
|---|---|---|---|
| **Soil Organic Matter Journals** | | | |
| Australian Journal of Soil Research | CSIRO Australia | 0004-9573 | 1963 |
| Biology and Fertility of Soils | International Society of Soil Science | 0178-2762 | 1985 |
| Canadian Journal of Soil Science | Agricultural Institute of Canada | 0008-4271 | 1921 |
| European Journal of Soil Science | British Society of Soil Science | 1351-0754 | 1950 |
| Geoderma | Elsevier* | 0016-7061 | 1967 |
| Plant and Soil | Royal Netherlands Society of Agricultural Science | 0032-079X | 1949 |
| Soil Biology and Biochemistry | Council of Biological and Medical Abstracts | 0038-0717 | 1969 |
| Soil Science | Rutgers University | 0038-075X | 1916 |
| Soil Science Society of America | Soil Science Society of America | 0361-5995 | 1936 |
| **Sedimentary Organic Matter Journals** | | | |
| Continental Shelf Research | Elsevier* | 0278-4343 | 1982 |
| Deep-Sea Research | Elsevier* | 0967-0637 | 1953 |
| Estuarine, Coastal and Shelf Science | Academic* | 0272-7714 | 1973 |
| Geochimica et Cosmochimica Acta | Geochemical Society | 0016-7037 | 1950 |
| Limnology and Oceanography | American Society of Limnology and Oceanography | 0024-3590 | 1956 |
| Marine Chemistry | Elsevier* | 0304-4203 | 1972 |
| Marine Geology | Elsevier* | 0025-3227 | 1964 |
| **Comprehensive Organic Matter Journals** | | | |
| Biogeochemistry | Kluwer* | 0168-2563 | 1984 |
| Global Biogeochemical Cycles | American Geophysical Union | 0886-6236 | 1987 |
| Organic Geochemistry | European Association of Organic Geochemists | 0146-6380 | 1978 |

*Denotes a publisher.

published both in books and special journal editions (e.g. Senesi and Miano, 1994). The EAOG presently has over 400 members, who are largely petroleum and marine organic chemists, and include about 1% soil scientists. The EAOG is affiliated with *Organic Geochemistry*, and hosts biannual meetings whose proceedings are highlighted in this journal. The OGD consists of an international group of predominantly petroleum and marine geochemists who meet annually and publish papers and proceedings in the journal, *Geochimica et Cosmochimica Acta*. Periodicals which often carry articles about organic matter in contemporary environments are listed in Table 2, and with few exceptions can be categorized as publishing studies on either soils or sediments.

The limited interaction between soil and sedimentary organic geochemists is evident not only from their largely separate societies, journals (Table 2) and meetings, but also from the lack of books and review articles encompassing both environments. We failed to find any reviews of the comparative organic geochemistries of soils and sediments. With a few exceptions (e.g. Zepp and Sonntag, 1995), most books and review articles on organic geochemistry are specific either to terrestrial or aquatic environments, with most exceptions being those dealing broadly with humic substances or universal processes such as mineral/organic interactions (Table 1 and Table 2).

## MESHED GLOBAL CYCLES

The roles of terrestrial and marine organic matter within the global carbon cycle are directly linked. A major thrust over the last two decades has been to define the global reservoirs and fluxes of organic matter (Fig. 1) and to more closely constrain the budgets and perturbations of biologically active elements. Although good progress has been made, many terms in these balances remain uncertain (Siegenthaler and Sarmiento, 1993). All carbon masses and fluxes will be expressed here in gigatons (Gt), where $1 \, Gt = 10^{15} \, g$ and is equivalent to a pedigram.

### Reservoirs

Greater than 99.9% of all carbon in the earth's crust is stored in sedimentary rocks (Berner, 1989). About 80% of this carbon (60 000 000 Gt) occurs within carbonates of limestones and dolomites (Hunt, 1996). The other 20% of total sedimentary carbon (15 000 000 Gt) is organic. The major organic form is kerogen, an insoluble macromolecular material that is disseminated at an average concentration of $\sim 1 \, wt\%$ in shales and limestones (Durand, 1980). Kerogens are derived from the biochemical remains of marine and terrestrial organisms which have been cooked to a plastic-like state in the earth (Tissot and Welte, 1978). Potential fossil fuels (coal and petroleum) account for $\sim 0.05\%$ of total sedimentary organic carbon (Hunt, 1996).

By far the largest pool of actively cycling carbon at the earth's surface (39 000 Gt) is dissolved inorganic carbon (DIC) in seawater (Siegenthaler and Sarmiento, 1993). The remaining surficial reservoirs each contain 500–1600 Gt of C world-wide, and individually hold 1–3% of the carbon in seawater DIC. At the beginning of the 1990s, atmospheric $CO_2$ comprised about 750 Gt of carbon, a value that is now rising at about 3.4 Gt C/yr
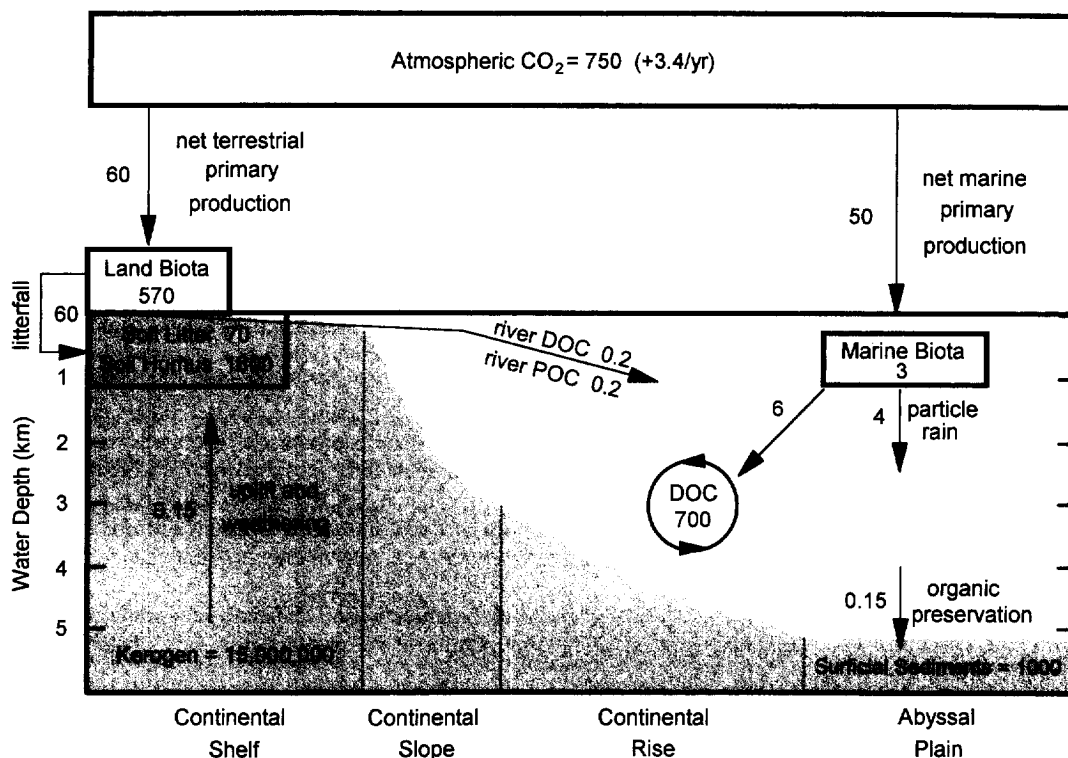
Fig. 1. Global reservoirs and fluxes of OC on land and in the ocean. Reservoir sizes and fluxes are given in gigatons of carbon (1 Gt = $10^{15}$ g) and Gt/yr, respectively, and rounded to 1–2 significant figures. Most data for river and marine systems are from Siegenthaler and Sarmiento (1993) or Hedges (1992). Terrigenous data are from Post (1993), except for the soil humus value of Eswaran et al. (1993). Not shown are rates of conversion of organic to inorganic carbon, and environmental fluxes of inorganic carbon.

(Siegenthaler and Sarmiento, 1993). Forms of organic carbon (OC) in the contemporary terrestrial environment (Fig. 1) include 570 Gt of terrestrial biota (~85% wood, 5% leaves and 10% ground vegetation), 70 Gt of plant litter on the soil surface (Post, 1993), and almost 1600 Gt of organic carbon within the top meter of soils (Eswaran et al., 1993). The latter estimate includes 360 Gt of OC in the top meter of peaty histosols, whose global carbon mass at greater depths is five to ten times larger (Adams et al., 1990). The major marine pools of reduced carbon (Fig. 1) are dissolved ( < 0.5 μm) organic carbon in seawater (700 Gt), plus a comparable amount of organic carbon in the top meter of marine sediments (Emerson and Hedges, 1988). Short-lived marine biota comprise only about 3 Gt of OC (Fig. 1). Overall, approximately 60% of all non-fossil OC is stored on land, where ~25% of the total resides in standing woody biomass.

### Fluxes

The global rate of net photosynthesis on land is estimated at about 60 Gt/yr, of which approximately 40%, 35% and 25% are incorporated on a global average basis into wood, tree leaves and

ground vegetation, respectively (Post, 1993). Total plant litter is produced at a similar rate, with about two-thirds being oxidized rapidly to $CO_2$ (Post, 1993). Division of the above carbon pool sizes by the corresponding global input rates gives mean residence times of roughly 20 years for tree woods, 4 years for ground vegetation and 1 year each for tree leaves and litter. In comparison, an input of approximately 20 Gt/yr of slowly degrading plant litter causes the soil humus pool to cycle about every 80 years. Approximately 0.2 Gt each of dissolved and particulate organic carbon (DOC and POC) are carried from land to sea annually by rivers (Fig. 1). Much of this riverine organic matter appears to be soil-derived (Meybeck, 1982; Hedges et al., 1994). Eolian fluxes of organic matter from land to sea are extremely difficult to constrain. They have been estimated to be < 0.1 Gt/yr (Romankevich, 1984).

Marine photosynthesis is carried out largely by single-cell phytoplankton, which produce organic carbon at a comparable rate to land plants (Hedges, 1992). Most phytoplankton are ingested by small zooplankton. Only ~10% of the net primary production escapes the upper 100 m of the

ocean in sinking fecal pellets and aggregated cellular debris (Fig. 1). The rain of POC out of the surface ocean attenuates exponentially down the water column due to respiration, and only ~10% of the sinking organic carbon reaches an average sea floor depth of 4000 m (Suess, 1980). Less than 10% of the deposited POC is ultimately preserved in the accumulating sediment (Jahnke, 1996; Wakeham et al., submitted). Global burial efficiencies of TOC exceed 0.1% (Fig. 1) only because >90% of sedimentary organic matter accumulates beneath shallower coastal marine waters (Berner, 1989).

DOC is extremely dynamic in the surface ocean, as indicated by a contemporary $^{14}C$ content (Williams and Druffel, 1987) and sharp concentration decreases in the upper few hundreds of meters of the water column (Benner et al., 1992; McCarthy et al., 1996). Most seawater DOC resides at about one ppm concentration in the deep ocean where it exhibits a $^{14}C$ content equivalent to an "age" of about 6000 years (Williams and Druffel, 1987). Division of the total amount of ocean DOC by this approximate mean residence time yields a "geochemical flux" through the deep pool of roughly 0.1 Gt OC/yr. Although this loss could be supported by the riverine DOC export rate of 0.2 Gt/yr, little compositional evidence exists for more than trace levels of terrigenous DOC in the open-ocean (Hedges et al., 1992; Opsahl and Benner, 1997), or for burial of "old" seawater DOC in excess of that in sediment porewater (Emerson et al., 1987).

The global burial rate of TOC in marine sediments is 0.1–0.2 Gt/yr (Berner, 1989). Up to half of this burial occurs in delta sediments, which in spite of large river inputs include large fractions of marine-derived organic matter (Keil et al., 1997). Most non-deltaic deposition is also adjacent to land (Hedges and Keil, 1995) on continental shelves (~0–100 m water depth) and continental slopes (~100–2000 m). Given a combined global discharge of TOC by rivers that is at least twice the burial rate of TOC in marine sediments (Fig. 1), and that sedimentary TOC is predominantly marine-derived (Hedges and Mann, 1979b; Gough et al., 1993), most organic matter introduced from land must be mineralized at sea. The ocean thus appears to operate as a net heterotrophic system by accumulating less sedimentary TOC than it receives via river discharge (Smith and Mackenzie, 1987). As a result of continuous degradation, leaching and erosion, almost no organic matter is preserved on land for geologic time scales.

Soils and marine sediments have thus been directly linked as key modulators of the global carbon cycle over at least the last 0.3 billion years since plants have covered the land (Berner, 1992, 1997). The steady flow of mass from continents to the ocean is attended by a sequence of changes in

the forms and compositions of the entrained organic materials. Kerogen in weathering sedimentary rocks is largely substituted in soils by humus, most of which in turn is replaced in delta and continental margin sediments by recently synthesized marine plankton remains (Hedges and Keil, 1995; Keil et al., 1997). Riverine dissolved organic matter (DOM) is not evident as a major component of marine sediments and therefore appears to be efficiently mineralized within the ocean (Hedges, 1992). Although concentrations of OC in sedimentary rocks and newly deposited continental margin sediments typically remain near 1 wt%, deep ocean deposits contain only 0.1–0.3% OC (Premuzic et al., 1982). For these sequential replacements and losses to occur, mechanisms for extensive mineralization of such difficult substrates as kerogen, lignin, humus and riverine organic matter must operate both on land and in the ocean. Coordinated studies by both soil and marine organic geochemists are needed to reveal the processes which selectively control organic matter transport and alteration from mountains to ocean sediments.

## CONTRASTS IN COMPOSITION AND PHYSICAL ENVIRONMENTS

### Soil environments

The different physical settings of mineral soils and surface marine sediments control the distributions and dynamics of the organic materials they incorporate. Soils are open systems that continually exchange materials and energy across their boundaries and within their matrices (Gerrard, 1981). Such dynamic systems seek steady state by balancing inputs and exports via internal system changes. The extreme environmental fluctuations which characterize the "excited skin of the subaerial segment of the earth's crust" (Nikiforoff, 1959) force pronounced heterogeneity and variability in soils over a spectrum of space and time scales.

Soils form where rocks, rainwater, atmospheric gases and living organisms first meet and interact (Berner and Berner, 1987). Rocks are fragmented by removal of overburden, changes in temperature and during transport by water and wind. Cation-rich minerals on the surfaces of exposed rock particles are weathered chemically by interaction with water, $CO_2$, and organic acids. The more soluble products of these interactions, such as NaCl and other salts, may be leached from the site of weathering and ultimately carried to the ocean. Insoluble minerals, such as crystalline quartz, aluminosilicates and iron oxides accumulate or form in situ. Over millennia, soil production by weathering is balanced by losses due to erosion. Given a mean continental denudation rate of 6.5 cm per thousand years (Berner and Berner, 1987), the global mean resi-

dence time of material in the upper meter of soils is roughly 15 000 years.

The rates and extents of soil formation are variable, depending on climate, biota, the parent rock, topography and the duration of pedogenesis (Jenny, 1941). In general, rates of soil formation increase with temperature and rainfall. Oxisols of the humid tropics are usually deep, strongly leached and rich in oxides of aluminum and iron. In wet temperate climates, strongly leached Spodosols develop which exhibit characteristic bleached layers. Under semiarid conditions downward movement of colloids is reflected by a clay layer at depth in Alfisols. In continental areas with hot dry summers, dark clay-rich Mollisols develop under grasslands.

The various soils are recognized by characteristic layering from the surface downwards. The layers are referred to as horizons and are recognized usually on the basis of color and clay content. A general example of the soil horizons associated with an uncultivated Spodosol is illustrated in Fig. 2. Spodosols exhibit a sequence of horizons created by strong leaching and acidity. The uppermost O layer consists primarily of accumulated plant litter overlying the mineral A horizon which is darkened in its upper (A1) portion by organic materials. The lower A2 horizon is evident as a bleached sand, the result of acidic and organic-rich percolating waters which wash both soluble and colloidal materials down the profile. The B layer is a zone of net accumulation, consisting of an organic-rich B1 horizon and a concentration of metal oxyhydroxides in the B2 horizon. The C horizon is weathered rock uninfluenced by pedogenesis.
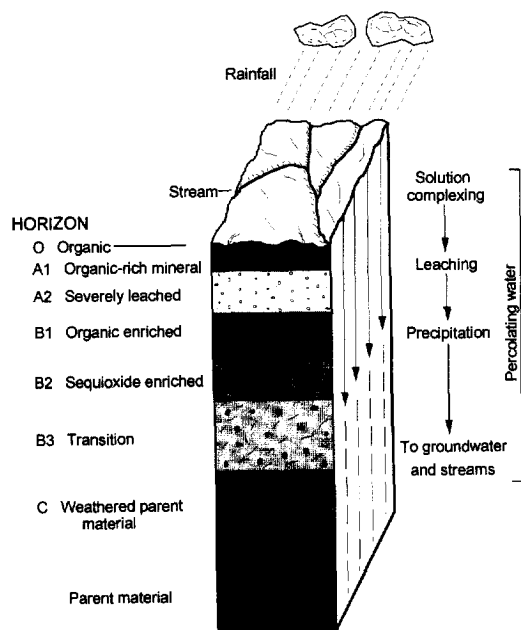
In arid basins, soluble products of weathering accumulate in the landscape and saline and sodic soils may result. In saline soils, NaCl and other salts create high osmotic potentials which prevent plants from taking up water at rates sufficient to maintain growth. Some saline soils are also alkaline due to the presence of $HCO_3^-$ and $CO_3^{2-}$ as counter ions to $Ca^{2+}$ and $Mg^{2+}$. Sodic soils contain a predominance of dissolved $Na^+$ over dissolved $Ca^{2+}$ and $Mg^{2-}$. Such soils are prone to dispersion of clay, which decreases permeability and eventually leads to unmanageable cultivation (tilth) and severe erosion (Nelson and Oades, 1996).

The solid inorganic products of rock weathering vary greatly in size and mineralogy (Fig. 3). The three basic *size classes* of small mineral particles in soils are clay ($<2\,\mu m$), silt ($2-20\,\mu m$ ISSS or 2–50 $\mu m$ USDA) and sand ($20-2000\,\mu m$ ISSS or 50–2000 $\mu m$ USDA), where ISSS = International Soil Science Society and USDA = US Department of Agriculture. The three fundamental *textural groupings* of soils can be classified based on their weight percentage of clay-size material (Oades, 1993) as sands ($<15\%$ clay), loams (15–35% clay) and clays ($>35\%$ clay). (To minimize confusion "clay" will be used hereafter in general reference to textural features and "clay mineral" will specifically denote layered aluminosilicates.) Quartz usually predominates in the sand-size fraction, whereas smaller particles consist increasingly of secondary minerals such as aluminosilicates and hydrous oxides of iron and aluminum. The smallest, often colloidal, mineral and organic particles comprise most of the surface area and ion-exchange capacity of soils and thus have a disproportionately large influence on physicochemical properties such as water content, shrinkage/swelling, ion composition and sorptive capacity.

In soils various single-grained particles are arranged into a hierarchy of aggregates (Fig. 3). Aggregates, which continually form and break down, are major determinants of soil "structure" and strongly affect processes such as water infiltration, aeration and drainage (Oades, 1993; Christensen, 1996). The smallest aggregates ($<20\,\mu m$) occur primarily as "stacks" of micron-size clay mineral plates (Murray and Quirk, 1980; Oades and Waters, 1991). Clay aggregates are maintained primarily by "bridging" of polyvalent cations ($Ca^{2+}$, $Mg^{2+}$, $Al^{3+}$ and $Fe^{3+}$) between negatively-charged clay crystals or organic colloids (Tisdall and Oades, 1982). "Microaggregates" ($20-250\,\mu m$) are formed from clay assemblages (Waters and Oades, 1991) plus mineral grains of comparable size (Christensen, 1996) and often surround a core of plant or fungal debris. "Macroaggregates" ($>250\,\mu m$) are formed by physical entanglement of coarse minerals and microaggregates by "sticky string bags" of living plant roots and fungal hyphae



Fig. 2. A generalized soil profile (after Stevenson, 1994).

| Scale (metres) | Primary Particles | | | Aggregations | Pores | Separation Method |
|---|---|---|---|---|---|---|
| | Mineral | Organic | Living | | | |
| $10^{-10}$ | Atoms | Atoms | | | MICRO-PORES | |
| $10^{-9}$ (nm) | Simple molecules | Simple molecules | | | Adsorbed and inter-crystalline water | |
| | Amorphous minerals | Poly-saccharides | | | | |
| $10^{-8}$ | | | (Viruses) | | | |
| $10^{-7}$ | Colloids | Colloids | | Organo-mineral colloids | | |
| | Clay | Microbial remains | | Quasi crystals | $\Psi$ < -15 bar | |
| $10^{-6}$ (um) | | Plant cell remains | Bacteria | Domains | MESO-PORES | |
| $10^{-5}$ | Silt | Pollen | Fungal hyphae | Assemblages | Plant available water | |
| | | | Root hairs Protozoa Nematodes | Micro-aggregates | | |
| $10^{-4}$ | Sand | Root remains | Roots | | $\Psi$ > -0.1 bar | |
| | | | | | MACRO-PORES | |
| $10^{-3}$ (mm) | | Straw | Ants | Macro-aggregates | Aeration | |
| $10^{-2}$ | Gravel | Woody remains | | | Fast drainage | |
| $10^{-1}$ | | | Tree roots Reptiles | Clods | | |

Separation methods (right columns): Gravity SPLITT, Centrifugal SPLITT, Field-flow fractionation

Fig. 3. Scale ranges in soil structure and biota (after Waters and Oades, 1991), as well as particle size ranges separable by different hydrodynamic sorting methods (see text).

(Oades and Waters, 1991). Loose macroaggregates increase soil tilth, but can be readily disrupted by biodegradation and cultivation (Beare et al., 1994).

The arrangement of various particles in soils creates a complex porous system filled with continu-ously changing ratios of water and air. Soils have porosities ranging from about 0.3–0.6, with 50% pore volume being an average value (Brady, 1990). Given an average mineral density near 2.6 g/cm$^3$, 50% pore space (porosity = 0.5) is equivalent to a

bulk (overall) density of roughly 1.3 g/cm$^3$ (Brady, 1990). The energy with which water is held in soil pores is measured in terms of soil water potential ($\psi$), which is expressed in negative bar or negative pascals (Pa), where $-1$ bar $= -100$ kPa (Papendick and Campbell, 1981). The potential of soil water depends on its microenvironment in the mineral matrix (Fig. 3). Water is tightly bound ($\psi <$ $-15$ bar) on particle surfaces and in pores $< 0.1-$ $0.2\ \mu$m in diameter. Water is held less strongly ($-15$ to $-0.1$ bar) in capillaries of $0.1-30\ \mu$m diameter. The upper limit of $-0.1$ bar represents the maximum capacity of soil to retain water against gravity. "Gravitational" water in pores $> 30\ \mu$m can drain freely, carrying solutes and colloidal materials through connected networks of macropores. Although most small pores in soils remain filled with water, larger pores contain water and air alternately. Waterlogging rapidly leads to anoxic conditions because the diffusion rate of $O_2$ is a factor of $10^4$ times slower in water than in air. Periodic precipitation and evaporation drive large variations in the water content of soils, which cause abrupt fluctuations in electrolyte concentrations, redox conditions and the activities of associated plants and microorganisms.

Soils are also subjected to large variations in temperature and pH. Average monthly temperatures in the top 10 cm of soils can vary by up to 30°C, with diurnal variations twice as great (Lynch, 1988). Most surface soils have pH values of 4.0–8.5 (Lynch, 1988). Highly leached soils may be extremely acidic after all bases have been removed. Soils in dry regions are generally more alkaline. At an individual site, pH typically increases downward as acidic $CO_2$ and dissolved organic substances released from roots and degrading plant litter are neutralized at depth by reactions with basic minerals. One consequence of extremely acidic conditions ($<$ pH 5) is the release of aluminum and manganese compounds which may be toxic to plants. Soils are thus highly heterogeneous and variable on essentially all space and time scales.

*Marine sedimentary environments*

In contrast to soils, surface marine sediments are relatively closed, constant, and persistent. Much of this constancy results from being covered by a thick blanket of water with an essentially invariant major ion composition and concentration. In addition to being continuously saturated with salty water, marine sediments are uniformly sodic due to high seawater concentrations of $Na^+$ versus $Ca^{2+}$ plus $Mg^{2+}$. Porewaters in marine sediments have pHs ranging from seawater values near 8, down to about 7 in deposits characterized by high rates of *in situ* respiration (Morse and Mackenzie, 1990). Most sediments depositing below 500 m water depth experience temperatures between $-1$ and 5°C

(Broecker and Peng, 1982). Less than 1% of incident sunlight penetrates to seawater depths of 100 m, confining radiant heating, photosynthesis and other photoreactions to surfaces of the shallowest sediments. Currents along the seafloor are usually on the order of tens of cm/s or less (Mooers, 1976), sufficient toward the upper range to resuspend sedimentary particles and breakup fragile aggregates, but not to fracture or abrade individual mineral grains (Bennett *et al.*, 1991).

The major mineral constituents of marine sediments have characteristic distributions in response to local river sources, plankton productivity and water depth. Most aluminosilicates, quartz and other lithic debris which comprise many coastal marine sediments (Thurman, 1988) were once soil components, with comparable textural distributions. Most of these particulate materials are introduced by rivers, flocculated rapidly by seawater and first deposited in estuaries and deltas. Up to half of this deltaic sedimentary material is repeatedly resuspended near the seabed, swept away and deposited in banded textural patterns over continental margins (Hedges and Keil, 1995). Globally, more than 95% of the total mass of suspended sediments discharged by rivers is deposited along continental margins (Berner, 1982).

Marine sediments also include remains of small calcium carbonate and opal shells of planktonic plants and animals. When not diluted by clastic minerals or dissolved away in ocean water, this biological debris can form oozes (Broecker and Peng, 1982) which collect on topographic highs (carbonates) and under productive ocean regions (opal). Shell-free sediments depositing in "red beds" beneath corrosive waters of the deep ocean consist mostly of clay-size particles that have been blown from arid land regions. Soil-derived materials thus occur over essentially the entire ocean floor, but are most concentrated near land and under central basins.

Surface marine sediments are less dense than soils. Porosities of fine-grained deposits range from 0.7–0.9 in the upper few centimeters and approach values near 0.5–0.6 at depths of a meter or more (Berner, 1980; Carpenter *et al.*, 1982). Fluvial particles are largely unassociated due to strong shear during flow and electrostatic repulsion at low ionic strength (Syvitski, 1991). Upon reaching estuaries, silt and clay minerals flocculate at salinities of 3– 5 g/l. Clay platelets initially aggregate edge-to-face, typically rearrange to an overlapping face-to-face orientation (Bennett *et al.*, 1991). Overburden from increased burial eventually leads to compaction (water expulsion) between crystal faces (Bennett *et al.*, 1991), leading to bulk densities at depth similar to those of soils. The higher porosities and looser packing of fine-grained minerals in surface marine sediments appear to derive largely from continuous

buoying of the component solids by sodic pore-waters favoring dispersion. The weaker associations among mineral grains in surface sediments versus soils should lead to a lower potential for physical shielding of sedimentary organic components, although such comparisons are rarely made in the scientific literature.

Being water-saturated and devoid of photosynthetic organisms, marine sediments only receive dissolved molecular oxygen from overlying seawater and become anoxic at depth. Essentially all ocean waters are oxic, except those at the bottom of restricted marine basins (e.g. the Black Sea) which presently cover < 1% of the sea floor. Dissolved $O_2$ concentrations are > 200 $\mu$M within 100 m of the ocean surface and in newly "downwelled" deep ocean waters (Fig. 1). Mixing of the underlying sediments by animals and currents can lead to intermittent oxygen penetration to depths of 10 cm or more (Aller, 1982). Such oscillations in sedimentary redox conditions may lead to more extensive remineralization of sedimentary organic matter than is possible under more static conditions (Aller, 1994). In contrast, dissolved $O_2$ concentrations can become quite low (< 20 $\mu$M) in the stratified ~200–800 m depth interval of temperate and tropical oceans (Broecker and Peng, 1982). Where this "oxygen-minimum layer" contacts the sea floor along upper continental slopes (Fig. 1), low bottomwater $O_2$ concentrations can severely limit oxygen diffusion, as well as sediment mixing (bioturbation) and seawater pumping (irrigation) by benthic animals. As a result, average penetration depths of $O_2$ into the surfaces of sediments usually are no more than a centimeter (Archer, 1990). Given sediment accumulation rates of millimeters per year on upper continental margins (Hedges and Keil, 1995), depositing particles are exposed to oxic sediment porewaters for 1–100 years. In contrast, open ocean sediments (typically depositing at rates of millimeters per thousand years under $O_2$-rich bottom-waters) often contain measurable porewater $O_2$ to depths of meters or more (Grundmanis and Murray, 1982) and hence more closely resemble unsaturated soils in their oxicity.

As a consequence of limited mixing and fluid exchange, and of receiving both reducing power (particulate organic matter) and dissolved oxidizing agents ($O_2$, $NO_3^-$, $SO_4^{2-}$, and $CO_2$) primarily from overlying water, marine sediments exhibit stepwise changes in redox conditions with increasing depth (Froelich et al., 1979). After dissolved $O_2$ disappears from porewater, denitrification occurs, followed by sequential reduction of $MnO_2$ to $Mn^{2+}$, FeOOH to $Fe^{2+}$, and $SO_4^{2-}$ to $HS^-$ (Stumm and Morgan, 1996). Due to the high sulfate concentration in seawater, most sediments do not advance to the more reducing conditions necessary for methanogenesis. The vertical scale of these redox transitions in surface marine sediments can range from millimeters to meters (Aller, 1994; Brandes and Devol, 1995). The presence of these sequential redox horizons in sediments, where accumulation and mixing rates can be measured radiometrically, allows the kinetics and stoichiometries of organic matter degradation to be determined. Such calculations are based on vertical profiles of dissolved and particulate compounds within intervals of the sedimentary matrix (Berner, 1980). These internal dynamics can be compared to delivery rates of sinking organic particles to the sea floor and to corresponding total fluxes of dissolved oxidizing agents and reduced products across the sediment–water interface (Jahnke, 1996). Combinations of such techniques allow detailed determinations of the reaction rates of bulk organic matter and many individual biochemicals for a variety of depositional settings where the specific electron acceptors, environmental conditions and types of microbial agents involved can be defined (Henrichs, 1992, 1993). Parallel studies in more open, heterogeneous and temporarily variable soil environments are extremely difficult.

## BIOLOGICAL DIFFERENCES

### Soil biology

One of the most unique and pervasive biological characteristics of terrestrial environments is the predominance of vascular plants as a source of organic matter to soils via litterfall and roots (Oades, 1993). Relative inputs by these two pathways vary with plant type, roots being more important for grasses than trees. It seems likely that up to half of the organic matter input to soils is through root systems of plants. Roots introduce organic matter by dying or sloughing tissue, rapid turnover of root hairs and exuding mucilages and soluble biochemicals directly into surrounding soil. This input helps sustain the rhizosphere, defined as the volume of soil immediately adjacent to root surfaces containing up to ten times more numerous and larger microorganisms than in nearby bulk soil (Bolton et al., 1993). In addition to being introduced by roots and leached from surface litter, fresh plant matter is often mixed into the soil by earthworms and other animals. Concentrations of organic matter therefore decline rapidly with increasing depth (Bolton et al., 1993). The pervasive injection of newly-formed photosynthate into soil profiles was reflected by rapidly increased $^{14}C$ concentrations within soil organic matter following widespread atmospheric testing of thermonuclear devices in the 1960s (Stout et al., 1981; Anderson and Paul, 1984; Harkness et al., 1994).

Vascular plants also affect the composition of soil organic matter by the biochemicals they uniquely produce (Oades, 1989; de Leeuw and Largeau, 1993). These include cutin, which covers the sur-

faces of leaves and stems, and suberin, which shrouds roots and occurs in barks (Kolattukudy, 1980, 1981). These two aliphatic polyesters account for 0.5–4% of the carbon in most nonwoody vascular plant tissues (Goñi and Hedges, 1990a). Lignins and tannins are also unique to vascular plant tissues, and impart a high aromatic carbon content. Lignins are phenolic macromolecules which comprise up to 40 wt% of total wood (Sarkanen and Ludwig, 1971). Tannins occur in soluble and insoluble forms (de Leeuw and Largeau, 1993) that have the common characteristic of vicinal phenols which readily oxidize to quinones and can combine with nitrogenous substances such as protein. The above biomacromolecules, plus cellulose and hemicellulose, occur in high percentages relative to protein in vascular plants, resulting in the characteristically high C/N weight ratios of woods (175–400), tree leaves (20–50), grasses and herbaceous plants (25–80) (Hedges et al., 1986; Lynch, 1988).

A large range of herbivores and detritivores feed on plant parts, both living and dead, so that a portion of photosynthate never reaches the soil. Plant debris is also mixed with soil by a variety of fauna, which generally do not extract more than 20% of the available energy. The remaining plant material is degraded by saprophytic microorganisms. The heterotrophic microorganisms involved consist predominantly of bacteria, fungi and actinomycetes (Metting, 1993). Estimates by a variety of methods, including microscopy, fumigation, respiration and ATP content, indicate that total microbial biomass accounts for a relatively constant 2–3% of soil organic matter (Jenkinson and Ladd, 1981). Bacteria predominate numerically over other types of microorganisms (Hassink et al., 1993), with numbers in typical temperate soils of $10^8$–$10^9$ per gram, compared to $10^7$–$10^8$ for actinomycetes and $10^5$–$10^6$ for fungi (Metting, 1993). Fungi, which are larger, usually constitute the dominant biomass component (Sparling, 1985).

Microorganisms are concentrated in surface soils (Nelson et al., 1994) where they usually occur in a quiescent state unless activated by the presence of water and available substrates. Although most soil bacteria are attached to particles, their distribution within the microarchitecture of the soil remains a matter of conjecture. Even if spread evenly in a one-cell deep layer, the $10^8$–$10^9$ bacteria/g typically present in clay loam would cover less than 0.1% of the total mineral surface (Adu and Oades, 1978). While well dispersed in bulk soils (Ladd et al., 1996), most bacteria occur in colonies distributed sporadically through the mineral matrix. Bacteria do not occupy pores less than three times their diameter (Hassink et al., 1993) and occur mostly in pores 0.5–5 µm in diameter (Foster, 1988). This restriction to voids greater than about 0.5 µm makes over 90% of the total pore space, in addition

to practically all surface area, in most soils inaccessible to bacteria and fungi (Van Veen and Kuikman, 1990; Hassink et al., 1993; Mayer, 1994a). The number of pores with diameters 0.5–5 µm increases with clay content, as does microbial biomass (Gregorich et al., 1991; Ladd et al., 1996).

Rather than being controlled by availability of appropriate pores, the activity of soil microorganisms appears to be limited primarily by lack of available organic substrate (Ladd et al., 1996). Basal respiration rates and biomasses of microorganisms therefore rarely correlate (Sparling, 1985). A predominantly inactive microbial biomass is also indicated by model-estimated average turnover times in natural settings on the order of 1.2–2.5 years, which are 3–4 orders of magnitude longer than for bacteria grown under optimal laboratory conditions (Jenkinson and Ladd, 1981). Being dispersed and essentially immobile, soil bacteria must wait dormant for the rare arrival of suitable substrate to their habitat. Particulate substrates must be degraded by exoenzymes to molecular units less than about 600 Da before they can be actively transported across cell walls by porins (Weiss et al., 1991). An exception to the situation of severe substrate limitation is the rhizosphere where microbial sizes, concentrations and activities are greatly elevated by continuous inputs of fresh organic matter.

Fungi are versatile and efficient degraders of soil organic matter, including more recalcitrant forms such as lignin, and can tolerate low pH conditions inhibitory to most bacteria and actinomycetes (Hobbie and Fletcher, 1988). Fungi are more tolerant of reduced water availability than bacteria, although all microorganisms suffer lowered metabolic function as capillary water is drawn from soil pores and becomes restricted to thin films on particle surfaces (Paul and Clark, 1989). Most fungi, however, are obligate aerobes and are relatively inactive in waterlogged soils and peats (Hedges, 1990). Compared to vascular plants, soil microorganisms are nitrogen-rich, with C/N weight ratios ranging from about 5:1 to 15:1 for bacterial- and fungal-dominated populations, respectively (Sparling, 1993). Retention of nitrogen during degradation of vascular plant tissues is thus a key strategy for terrestrial microorganisms. Because nitrogen is limiting for vascular plant production in most soils (Paul and Clark, 1989) and occurs predominantly in organic form (Tate, 1987), the mineralization rates of litter and humus largely govern the productivity of unfertilized vascular plants that do not fix nitrogen.

## Sediment biology

The biology of marine sediments is quite different from that of mineral soils. With the exception of seagrasses growing in shallow water, vascular plants are absent from the ocean. Phytoplankton dominate

in the sea, where their production is usually limited by low concentrations of dissolved nutrients or light. High phytoplankton concentrations (blooms) occur in restricted regions where nutrient-rich seawater is introduced from depth into the upper 100–200 m of lighted surface waters. Regions of persistent nutrient upwelling, such as off Peru, are rare and account for ~0.1% of the total ocean surface (Smith and Kalber, 1974). Sediments underlying these highly productive regions receive greater rain rates of fresh particulate organic matter and resemble the dynamic rhizospheres of terrestrial systems.

Bacteria are the primary degraders of sedimentary organic matter. Low $O_2$ availability and continuous water saturation severely limit most fungi (Lynch, 1988). Bacterial numbers in surface marine sediments ($10^8$–$10^{10}$ cells/g dry wt) resemble those in soils and also decrease by about an order of magnitude downward within the first 10 cm of these deposits (Deming and Baross, 1993). Also as in soils, living bacterial carbon in sediments increases with the concentration of TOC, of which it comprises about 1% (Hobbie and Fletcher, 1988). Bacterial carbon correlates more strongly with particulate organic matter input to the seafloor than with water depth, temperature or TOC. Thus sedimentary bacteria, like their soil counterparts, appear substrate limited (Deming and Baross, 1993). One consequence of prominent sulfate reduction is that organic matter in diagenetically active surface sediments is often exposed to high concentrations of sulfide and polysulfide, both of which can add across double bonds in vulcanization-type reactions to form organosulfur compounds (e.g. Kohnen et al., 1989). Because fermentative bacteria, upon which sulfate reducers depend for dissolved substrates, have difficulty degrading lignin and substances containing long alkyl chains, these types of carbon-rich materials tend to accumulate in anoxic marine sediments (Hedges and Keil, 1995).

Information on physical distributions of bacterial cells within the microfabric of marine sediments is sparse. This may result in part because particles in sediments are not as strongly associated as in soils, making microenvironments less definite and consequential. In addition, the challenges of labeling and visualizing microorganisms in a loosely associated mixture saturated with saltwater are substantial. It is evident, however, that most sedimentary bacteria are attached to particles (Rheinheimmer, 1992). Both field and theoretical studies suggest that sedimentary bacteria are not supported either by direct contact with particulate substrates or by dissolved organic substances passively diffusing from bulk porewater. Rather, substrates are thought to be obtained by individual bacteria secreting extracellular enzymes into a "foraging sphere" about 5 $\mu$m in radius about the cell (Vetter et al., submitted). The exoenzyme diffuses out into the matrix to reach a particulate biomacromolecule from which it releases low-molecular-weight hydrolysis products, a portion of which diffuse back to the cell. A net gain of energy to the bacterium is most likely if the "expensive" exoenzyme binds tightly to the target biopolymer and continues to release hydrolysis products until the source is depleted. Consistent with this theory is the observation that bacterial numbers in sediments of different texture and porosity nevertheless remain almost constant at a value of about one bacterial cell per 100 $\mu m^3$ of porewater (Schmidt et al., submitted—a). It remains to be seen how different these foraging strategies might be from those of microorganisms living in soils, where exchange of dissolved solutes and air in capillaries is active due to rapidly varying water content.

These very different biological systems lead to a number of contrasts in the composition and dynamics of marine versus terrestrial organic matter. Due to the dearth of lignin and other nitrogen-free structural biopolymers, protein-rich marine plankton have an average C/N ratio near 6 (Redfield et al., 1963). The absence of lignins and tannins makes marine-derived organic matter more aliphatic on average and less prone to immobilize nitrogen by tanning-type condensation reactions. Given, in addition, the absence of percolating water in marine sediments, strategies for nitrogen conservation during metabolism are not so stringent as for terrestrial systems. The low concentrations of resistant biopolymers in most phytoplankton also make direct feeding by small animals more feasible, favoring herbivory versus saprophytic breakdown as the principal first stage of organic matter degradation at sea. In addition, most organic turnover occurs in the water column, so that materials which first contact marine sediments are at a more advanced stage of degradation than plant litter and exudates in soils. Although labile plankton remains are periodically mixed into surface marine sediments by animals, direct injection of large amounts of fresh organic materials by invasive plants and percolating water is unique to soils.

## METHODOLOGICAL CONTRASTS

### Soil holism

The different physical settings and economic uses of soils and sediments have led to contrasting trends in fundamental approaches to their study. In spite of their complexity and physicochemical variability, soils can be readily sampled, monitored and manipulated. Variations in temperature, moisture, electrolytes, gases, and biota can be induced on scales from millimeters to meters. Many soils also have known histories of usage which allow comparative studies of carbon turnover following per-

turbations such as changes in predominant vegetation between ^{13}C-poor C3 (e.g. trees or cereal grains) and ^{13}C-rich C4 (e.g. corn or sugar cane) plants (Balesdent et al., 1987; Skjemstad et al., 1994a). Pesticides, herbicides and other anthropogenic compounds, which often have been added to soils in known amounts and chronologies, can serve as extremely useful models for predicting the environmental fates of chemically similar natural products (Beck et al., 1993; Mansour, 1993). Paleosols are also available, sometimes in extensive sequences such as Chinese loess deposits (Curry et al., 1994), for study of ancient earth surfaces.

One of the major thrusts of soil science had been to understand and maintain the complex interactions of processes and conditions affecting crop production. The resulting need to deal with soils as interactive whole systems has created a strong emphasis on organic components that directly affect the bulk properties and functions of soils (Gregorich et al., 1994). Thus, soil organic analyses tend to be quantitative, focused on major constituents, and made in conjunction with measurements of other system properties such as microbial biomass, plant growth response and soil physical characteristics. Because many of the processes of interest pertain to fertility, emphasis has been on characteristics and distributions of organic substances within the zone of root growth, as opposed to deeper processes or leakage of materials to groundwater and streams. For the same reasons, measurements which reflect relatively fast system responses on a seasonal to decadal scale have been emphasized over those occurring over centuries to millennia.

Given this holistic approach to practical short-term applications, it is not surprising that studies of soil organic matter are based strongly on measurements of bulk chemical properties (e.g. % OC, C/N, $\delta^{13}$C, $\delta^{15}$N) and broadly defined chemical functionality as reflected by spectral (e.g. IR, NMR, ESR) analyses (Oades, 1989). Humus and humic substances have received attention as major forms of soil organic matter related to bulk properties such as cation-exchange capacity, water-holding capability and soil structure. While chemically drastic, base extraction is one of the few simple treatments by which major components of total soil organic matter, such as humic acids, can be readily isolated from the mineral matrix for detailed characterization. When biochemicals are analyzed, emphasis has been on compound types such as carbohydrates which constitute major precursors or components of soil organic matter (Cheshire, 1979).

During the last 20 years there has been a shift from detailed chemical descriptions of soil organic matter to attempts to understand the entire system in terms of integrated physics, biology and chemistry. Development of techniques for measuring microbial biomass in soils, particularly the fumigation/extraction procedure (Jenkinson and Ladd, 1981), has led to considerable efforts to understand the role of biota in soil organic matter forms and functions. Other major developments have involved defining the distribution of organic materials within the soil matrix by direct observation using histochemical procedures combined with microscopy (e.g. Foster, 1985) and various physical fractionations of soil components prior to analysis (Christensen, 1992, 1996).

## Sediment reductionism

In contrast to soils, surface marine sediments occur in remote environments that are not easily sampled or manipulated and have limited direct economic applications. One of the main practical reasons to study organic materials in modern marine deposits is their ability to record and integrate events in remote water columns which are difficult to observe directly over time. A second, related purpose has been to recognize the depositional setting where organic-rich sediments form, so that petroleum can be more successfully found within ancient rock counterparts deep in the earth Hunt, 1996). In both of these applications bulk properties of sediments need not be considered in detail. The thrust has been to recognize individual compounds which are specific to key biological sources or environmental conditions. These diagnostic biomarkers typically are minor components, with little direct influence on the bulk properties of total organic matter mixtures (Hedges and Prahl, 1993). Lipid biomarkers have received special attention because they are easily extracted, source-specific and have recognizable derivatives in ancient rocks and petroleums. Many biomarker applications are qualitative (yes/no) or relative (more/less) and do not necessitate absolute quantitation. "Fingerprinting" within a compound class via chemolytic or pyrolytic degradation is often sufficient.

Although often not broadly representative, the biomarker approach so typical of marine studies has a number of intrinsic advantages. One of these is high information potential resulting from the great number and structural diversity of individual molecule types that can be analyzed at one time. Unique structural traits often can be traced along extended reaction sequences such as has been done for chlorophylls/porphyrins (Baker and Louda, 1986), carotenoids (Repeta and Gagosian, 1987) and steroidal compounds (de Leeuw and Baass, 1986). Biomarkers of many different biological and geographic sources have now been recognized, and molecular indicators of past environmental salinities, temperatures and oxicities also exist (Johns, 1986; Brooks and Fleet, 1987). Another advantage is sensitivity, because organic compounds can be quantified at concentrations that are orders-of-mag-

nitude lower than would be evident from only bulk measurements (Hedges and Prahl, 1993). With the advent of isotope-ratio-monitoring gas chromatography/mass spectrometry (irm-GC/MS), the source specificity of biomarkers has been greatly enhanced by simultaneous stable carbon isotope analysis on nanogram amounts of eluting compounds (e.g. Hayes et al., 1990; Lichtfouse et al., 1994a; Sinninghe Damsté et al., 1995).

Because biomarker measurements can be made on bulk sediments whose other properties are often of little concern, physical fractionations and microscopic observations of marine samples have been low priorities. Due to this "find em and grind em" approach, effects of the forms and microenvironments of sedimentary organic materials are just beginning to be systematically addressed. This is unfortunate because selective hydrodynamic sorting during offshore transport, and the extreme effects of particle size and location in diffusion-limited aqueous environments, have pronounced effects on the distributions and dynamics of organic matter.

Studies of modern marine sediments as models for the types of environments in which petroleum source rocks once formed has also shaded investigative approaches for contemporary sediments. One result has been a strong emphasis on extremely organic-rich deposits accumulating under low-oxygen or anoxic bottomwaters (Tissot and Welte, 1978), even though in the modern ocean such deposits account for only 1% of all organic matter burial (Berner, 1989). In addition, attempts to simulate geothermal heating in laboratory experiments have led to extensive information on the effects of high temperatures on sedimentary organic matter in the presence of water (Siskin and Katritzky, 1991; Lewan, 1993) and different mineral catalysts (Eisma and Jurg, 1969; Simoneit, 1993). Interest in kerogens, whose thermal breakdown deep in sedimentary rocks is the major source of petroleum, also has driven the search for possible precursors and formation pathways. One outcome of these studies has been the discovery in vascular plants and microorganisms of a wide range of hydrolysis- and degradation-resistant biomacromolecules (Tegelaar et al., 1989; de Leeuw and Largeau, 1993) which can contribute "ready-made" kerogens to modern sediments. Macromolecules made by the spontaneous condensation of sulfides with unsaturated lipids and other biochemicals also are being extensively studied as potential kerogen precursors (Kohnen et al., 1991; Hofmann et al., 1992).

## A COMPARISON OF SOIL AND SEDIMENTARY ORGANIC MATTER

### Organic matter concentrations and controls

Concentrations of OC in both soils and sediments represent a dynamic balance between biomass input and its export and mineralization. Despite great differences between their physical settings and indigenous biota, average weight percentages of nonliving organic matter in both soils (Oades, 1988; Schnitzer, 1991) and surface marine sediments (Premuzic et al., 1982; Jahnke, 1996) are typically in the range of 0.1–5 wt% (Fig. 4). The regional patterns of organic carbon distribution in soils and sediments, however, are quite different. In the following discussion, all living and dead reduced-carbon compounds within the mineral matrix of soils are referred to as "soil organic matter" (Paul and Clark, 1989). "Humus" is amorphous soil organic matter remaining after recognizable fragments of biological material have been physically removed.

Organic contents of soils (Fig. 4A) and surface marine sediments (Fig. 4B) exhibit contrasting areal patterns that are thought to be controlled by different processes. While the phosphate content of the parent rock provides some constraints (Tiessen et al., 1984), precipitation and temperature are among the major controls on soil organic concentrations (Jenny, 1941; Post et al., 1985). Parton et al. (1987, 1993) found that the OC content of temperate grassland soils could be modeled using moisture, temperature, texture and plant lignin levels as master variables. In general, increased precipitation leads to elevated organic matter input as the net result of greater stimulation of plant production versus microbial respiration. For every 10°C increase in mean annual temperature, soil organic matter content decreases by a factor of 2–3, due primarily to increased microbial respiration (Jenny, 1941). Elevated organic concentrations are also found for finer-textured soils receiving greater fractions of plant material with high lignin/nitrogen ratios. Similar results have been obtained for temperate forests (Pastor and Post, 1986), agricultural lands (Jenkinson, 1990), tropical regions (Parton et al., 1987) and world soils (Schimel et al., 1994). Overall, soil organic matter storage is lowest in warm deserts and greatest in cool, wet environments (Post et al., 1985; Post, 1993) and thus exhibits a strong latitudinal and altitudinal dependence (Fig. 4A). Overall, the same variables of temperature and precipitation that largely determine soil type and vegetation also determine soil organic content, linking all these landscape manifestations in conceptual constructs such as Holdridge life-zone classifications (Fig. 4A). Soil texture and land use also come into play (Schimel et al., 1994), with cultivation of forest or prairie soils resulting in a decrease of organic content of 50% or more (Davidson and Ackerman, 1993; Scholes and Scholes, 1995).

In contrast to latitudinal patterns of distribution on land, organic matter in marine sediments tends to be focused on continental margins (Fig. 4B) in patterns which also provide clues to controlling
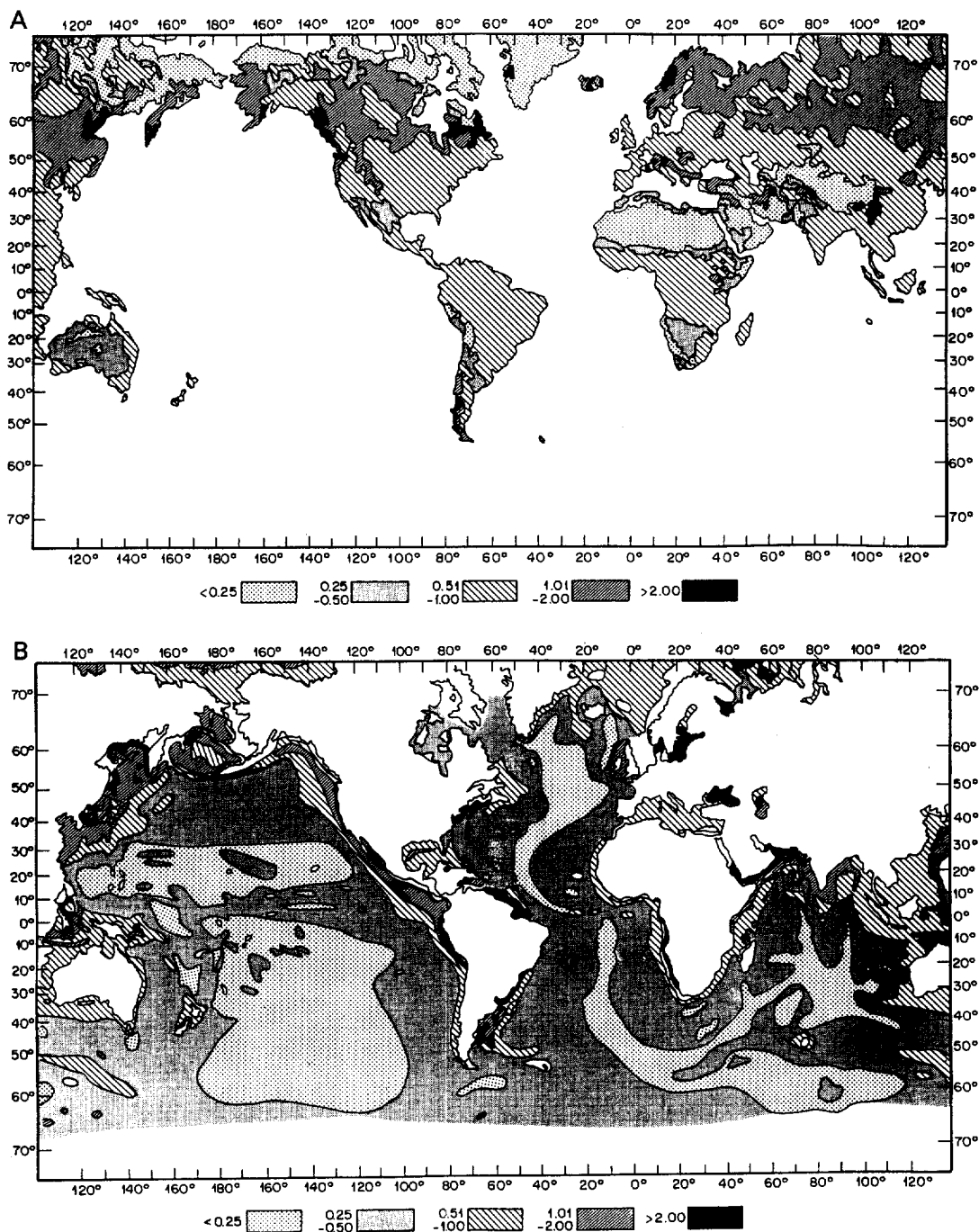
Fig. 4. Weight percentages of OC in (A) contemporary soils (see below) and (B) surface marine sediments (the latter from Premuzic et al., 1982). The plot of weight percent OC in surface (0–100 cm average) mineral soils of the world was generated by Emilio Mayorga using a geographic information system. The areal distributions of Holdridge Life Zones (digital raster map at 0.5 degree resolution; Leemans, 1992) and the total OC storage (kg $C/m^3$) typical of individual zones (Post et al., 1985) were used together to estimate average inventories of OC stored to a meter depth across the globe. Each kg $C/m^3$ was then normalized to the corresponding bulk density of each soil as calculated from its texture (digital raster map of wt% sand, silt and clay at 1 degree resolution from Zobler, 1986 and Staub and Rosenzweig, 1992) to determine a weight percentage of OC. This conversion was made using the porosity/texture relationship of Saxon et al. (1986) and an assumed mean density of 2.65 $g/cm^3$ for soil minerals.

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processes. The low extreme of the range (0.1–0.2% OC) is occupied by fine-grained sediments depositing beneath well-oxygenated water over huge areas of the deep open ocean. These pelagic sediments, along with dessert sands and loess beds (Curry *et al.*, 1994), are among the most organic-poor mineral deposits on Earth. The other extreme is represented primarily by marine sediments depositing in anoxic basins or where oxygen-poor waters impinge on sediments along upper continental slopes (200–1000 m water depth). Such organic-rich deposits are the marine counterparts of peats and reach especially high organic concentrations beneath productive zones such as the Peru and southwest African coasts. Intermediate concentrations in the range of 0.5–3% OC are typical of sediments depositing within deltas and upper continental margins, where >90% of all carbon burial occurs. Within these marine regions, and in parallel to most soils, an inverse relationship between the organic content and grain size of sediments is usually observed (Premuzic *et al.*, 1982; Mayer, 1994a,b; Keil *et al.*, 1994c).

As with soils, there have been many attempts to relate the carbon contents of surface marine sediments to local environmental variables. No factor, however, has proven universally diagnostic for marine deposits, in part because most parameters used to measure organic preservation, such as % OC and input/burial ratios, are subject to independent processes such as dilution by minerals and sediment resuspension. Environmental variables which are most commonly considered to be important include plankton productivity, the $O_2$ content of bottomwater, and sediment accumulation rate and texture (Henrichs, 1992, 1993; Tromp *et al.*, 1995). Separating these various factors in a meaningful way has been difficult. For example, elevated productivity in surface marine waters eventually leads to lowered $O_2$ content of underlying bottomwater, and to faster sediment accumulation rates when shells are preserved. These changes result in reduced periods of exposure of accumulating organic matter to high concentrations of microorganisms and $O_2$ near the sediment surface.

The two main variables affecting organic concentrations in soils, temperature and water availability, are essentially invariant for marine sediments. Some common trends, however, do exist between environments. In both settings, greater organic concentrations correspond to waterlogged, oxygen-poor conditions, whereas low concentrations are typical of coarse-grained systems. High local primary productivity also favors larger organic inventories in both soils and sediments. This trend is especially pronounced on land where plant materials are directly introduced throughout the soil, as opposed to being extensively degraded during transit to the sea floor (Berger *et al.*, 1988). Degradation-resistant

biomacromolecules occur in both vascular land plants (e.g. lignin and tannin; de Leeuw and Largeau, 1993) and marine plankton (e.g. algaenans; Gelin *et al.*, 1996) at concentrations sufficient to substantially augment OC accumulations.

Parallel trends toward higher organic concentrations in finer-grain soils (Schimel *et al.*, 1994) and continental margin sediments (Premuzic *et al.*, 1982) suggest a common textural effect. When soil particles are separated by size, either fine silt (2–5 μm) or clays (<2 μm) contain the highest % OC, with enrichments up to a factor of ten (Christensen, 1996). This pattern is illustrated in Fig. 5A for various size particles from partially dispersed surface soils (Turchenek and Oades, 1979). Conversely, sand-size particles (>20 μm) usually contain less than 10% of soil OC. For unknown reasons, the extent of enrichment of OC in both the clay and silt fractions varies inversely with their weight percentages in the total soil (Christensen, 1992).

Elevated % OC values of fine silt fractions in many soils could result either from proportionately greater input of organic matter or unusual stability.
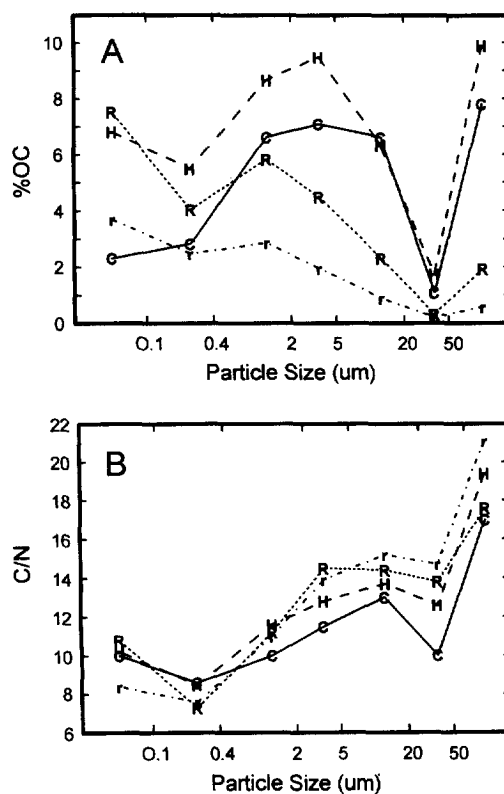


Fig. 5. Values of (A) % OC, and (B) the corresponding C/N weight ratios, C/N, plotted for different particle size fractions separated from A horizons of three different soils. All data are from Turchenek and Oades (1979). The three soils are of the Haploboroll (H), Calciaquoll (C) and Rhodoxeralf types, the latter before (R) and after (r) cultivation.

One factor contributing toward such high organic contents may be that bacterial biomass is concentrated in these intermediate-size particles (Van Veen and Kuikman, 1990). Although living microbes comprise only a few percent of total soil carbon, their remains may concentrate in the aggregates they colonize (Tisdall and Oades, 1982). Adsorption of organic matter to surfaces of the small component particles, and binding of small aggregates together by iron oxides and resistant humified organic matter, may also enhance organic concentration. Small (10–100 μm) "cores" of plant debris occluded with adhering mineral particles have been found in a variety of soils where they contribute



Fig. 6. Two plots of % OC versus specific surface area (SSA) analyzed by the $N_2$-BET method. Part A is for size fractions (<0.2, 0.2–2, 2–20 and 20–2000 μm) of surface soils analyzed by Feller et al. (1992). Progressively finer size fractions with greater SSA values are indicated by larger numbers in the series 1–4. Lines join size fractions from the same soil. Corresponding data (indicated by w) for similar analyses of whole surface soils were taken from Mayer (1994b), Gallez et al. (1976) and Borggaard (1982). The shaded areas in both plots indicate the organic loading range typical of surface marine sediments from upper coastal margins and corresponds roughly to that theoretically expected for a monolayer-coating of organic matter onto mineral grains (Mayer, 1994a). Part B illustrates data for different size fractions of particulate material suspended in the lower Columbia River (R) and from surface sediments collected in the plume (P), mid-shelf silt deposit (S), $O_2$-minimum zone (M) and outer slope (L) of the Washington State continental margin (Keil et al., 1994c).

substantially to total organic matter (Golchin et al., 1994a,b).

The observation that % OC is not consistently higher for smaller particles in soils (Fig. 5A) suggests that surface area alone does not explain OC distributions, as would be expected if most organics were sorbed to mineral surfaces in uniformly thick coatings (Mayer, 1994a,b). This inference is supported by a plot (Fig. 6A) of % OC versus specific surface area (SSA) for various size fractions (<0.2, 0.2–2, 2–20 and 20–2000 μm) of five surface soils (Feller et al., 1992). Also illustrated for comparison is the organic loading range of 0.5–1.0 mg $OC/m^2$ SSA to be expected for one-molecule-thick organic coating of all mineral surfaces (Mayer, 1994a,b), excluding interbasal faces of swelling clays (Keil et al., 1994c). Maximal OC concentrations occur in the 2–20 μm size fraction for four of the five soils, with progressively lower carbon contents for finer material with higher SSA. Many of the coarse soil fractions have % OC values in substantial excess of a "monolayer" equivalent, whereas the fine fractions (SSA > 45) have % OC values falling within or slightly below this zone. Data for whole soils from Mayer (1994b) and others exhibit similar trends (Fig. 6A). Mayer's bulk soils with elevated % OC/SSA ratios contained abundant low density (<1.9 g/ml) organic debris. Plant debris probably explains the high % OC values of many sand and silt fractions. Although some of the analyzed soils and soil fractions contain measurably less than a monolayer-equivalent loading of organic matter (Fig. 6A), large deficits are rare.

In marine sediments, textural control of organic concentrations was suggested by early studies in which the % OC of bulk marine sediments was found to increase with decreasing mean particle size (Suess, 1973; Tanoue and Handa, 1979; Mayer et al., 1985). This hypothesis was later supported by direct correlations between % OC and SSA for whole sediments (Mayer et al., 1988; Mayer, 1994a,b) and sediment size fractions (Keil et al., 1994c; Bergamaschi et al., 1997) collected from different coastal regions with contrasting depositional conditions (Fig. 6B). The bulk of the sediment data fall within the interval of 0.5–1.0 mg $OC/m^2$, corresponding to "monolayer-equivalent" organic loading. The actual distribution of the organic matter on mineral surfaces, however, is presently unknown. As with soils, elevated organic concentrations are often seen in sediment size fractions with low surface areas and abundant coarse plant debris (Keil et al., 1994c). Physically separable discrete organic debris, however, usually accounts for less than 10% of TOC in continental margin sediments (Hedges and Keil, 1995). Sediments accumulating beneath highly productive coastal oceans with bottomwaters strongly depleted in $O_2$
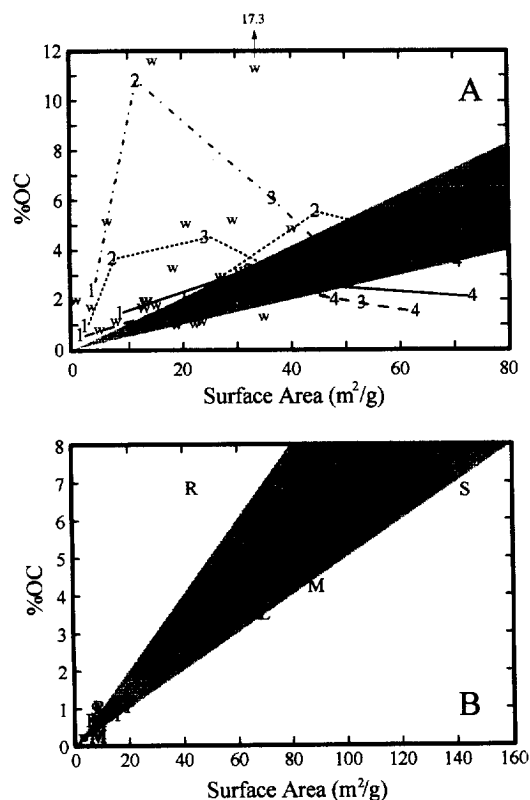
( < 20 $\mu$M) also exhibit consistently elevated % OC/ SSA ratios, but typically at OC loadings 3–5 times higher than for more oxygenated continental margin deposits (Hedges and Keil, 1995; Bergamaschi et al., 1997). Whether such organic-rich accumulations might be due to thick molecular coatings, minimal bioturbation and/or high sulfide concentrations is uncertain.

Evidence that association with minerals strongly affects the amount of organic matter preserved in coastal sediments comes from an experiment where 25–50% of the sedimentary OC was desorbed (sequentially by seawater, distilled water and KCl) from different horizons of marine sediments up to 500 years in age (Keil et al., 1994b). When given as substrate to aerobic bacteria, at least 70% of the desorbed DOC was mineralized within 5 days. As Nelson et al. (1994) found for soils, a major fraction of bulk sedimentary organic matter appears to be intrinsically reactive, but physically protected by association with mineral material. Because particles in sediments are less strongly associated than in soils, sedimentary organic matter is more likely to be protected by sorption to particle surfaces than from occlusion between particles. Because mineral grains have most of their surface area in pores too small for access by microorganisms or their exoenzymes (Mayer, 1994a), strongly sorbed organic molecules can be protected without the need for high intrinsic stability or extensive particle aggregation.

Sorting out why modern open ocean sediments typically have 5–10 times lower % OC levels than expected from coastal counterparts with equivalent surface areas (Hedges and Keil, 1995) has been challenging. Low plankton productivity, long water columns, slow sediment accumulation rates and deep penetration of $O_2$ into these deposits may all be involved (Emerson et al., 1987). It is clear from the example of turbidite deposits, however, that sedimentary organic matter can be mineralized to low levels simply as a consequence of long-term exposure to porewater $O_2$. Deep-sea turbidites are formed when large sediment masses slump from topographic highs, flow along the sea floor as dense currents and spread to form extensive deposits on adjacent abyssal plains. Turbidites formed by slumping from continental slopes are often finegrained, vertically uniform and organic-rich (Weaver and Thomson, 1987). Although initially homogeneous, such turbidites react with $O_2$ diffusing in from bottomwater to form sharp "oxidation fronts" which slowly penetrate into the deposit. These clearly visible interfaces provide adjacent "before" (below) and "after" (above) examples of the effect of $O_2$ on sedimentary organic matter, without many of the complications such as intense mixing and changing inputs which often compromise comparisons among incrementally accumulating sediments (Thomson et al., 1993).

The most studied turbidite to date is a relict 4-m thick sequence deposited on the Madeira Abyssal Plain off Northwest Africa about 140 000 years BP (Prahl et al., 1989; Cowie et al., 1995). During the first 10 000 years after deposition, $O_2$ "burned" into the top 50 cm of the deposit. Another turbidite then capped the first and cut off $O_2$, after which the entire sequence returned to anoxic conditions. Comparison of samples from above and below the oxidation front shows that % OC values dropped from about 1.0% in the deep (unreacted) horizon to near 0.2% in the top (oxidized) samples (Cowie et al., 1995). Pollen contents of the same sediments decrease from ~1600 grains/g initially to zero pollen in the oxidized horizon (Keil et al., 1994a). The latter observation is mechanistically telling because pollen is degradation resistant and nondiffusive. Thus 80% of the total organic matter and all pollen that was preserved for 140 000 years in the anoxic deeper portion of the turbidite was mineralized in situ within 10 000 years or less when exposed to dissolved molecular oxygen. The % OC of the oxidized turbidite horizons is similar to modern sediments now forming in the deep ocean, indicating that slow oxic degradation is sufficiently severe alone to account for their extremely low organic contents (Fig. 4).

Why then might protective sorption be largely overcome by oxic degradation in the deep ocean? The answer may lie in offshore increases in the time that sedimentary organic matter is exposed to porewater $O_2$, and in the reaction kinetics of different organic materials under oxic versus anoxic conditions (Hedges and Keil, 1995). Oxygen exposure time in the surface horizons of marine sediments is roughly equal to the depth of $O_2$ penetration into the deposit divided by the sediment accumulation rate. Oxygen penetration depths increase offshore from typical values of 1–5 mm on continental shelves, to 5–50 mm on lower continental slopes, and > 50 mm in deep-sea sediments (Archer, 1990). Corresponding sediment accumulation rates decrease seaward from roughly 1–10 mm/yr (shelf), to 0.01–1 mm/yr (slope) to 0.001–0.01 mm/yr (abyss). As a result, oxygen exposure times increase offshore from the order of years to centuries to millennia (Hedges and Keil, 1995). Thousands of years of $O_2$ exposure were sufficient for the Madeira turbidite, and probably most deep ocean sediments, to cause profound losses of organic matter. On upper continental margins, $O_2$ exposure times may not be sufficiently long for a slow oxidative process to have an appreciable effect. A pronounced decrease in sedimentary concentrations of OC and pollen at about 2–3 km water depth along the Washington State continental margin (Keil et al., 1994a) suggests a transition from sorptive protection to slow oxic degradation of organic matter may occur near this interval. Slow, but extremely severe, oxic

degradation also may take place at shale and coal outcrops, and in well aerated soil, and could help explain the previously noted turnover of such resistant materials in the global carbon cycle (Hedges, 1992).

*Organic matter compositions*

The makeup of organic matter in soils and sediments can be measured at a variety of scales ranging from isotopic, elemental and functional group compositions to the absolute concentrations of different organic molecules and their stereoisomers. In general, analyses of small structural units such as isotopes and elements are broadly representative of the entire organic mixture, but provide few descriptive characteristics. Degradation of macromolecules (by hydrolysis, chemolysis or pyrolysis) into diverse structural units amenable to sensitive chromatographic quantification can yield large amounts of information, but often on only a small and potentially unrepresentative fraction of bulk organic mixtures. Non-destructive analyses of interatomic bonding patterns, such as are obtained by spectral methods (e.g. IR and NMR), represent a revealing compromise between chemical detail and representativeness.

*Biochemical compositions* of individual soils and sediments are seldom determined comprehensively, largely because of the great number of specific analyses required. Based on scattered characterizations of many surface soils, an average makeup of roughly 10–20% carbohydrates, 10% nitrogenous biochemicals and 5–15% lipids has been estimated (Oades and Ladd, 1977; Schnitzer, 1991). Measured carbohydrates include aldoses (5–15%), uronic acids (1–5%) and amino sugars (2–6%). Nitrogenous biochemicals are largely amino acids (Stevenson, 1994). Soil lipids include fatty acids, fatty alcohols and hydrocarbons, as well as phospholipids and lipopolysaccharides derived from microbial biomass (Stevenson, 1994; Zelles *et al.*, 1995). Comparable analyses of modern coastal marine sediments indicate 10–15% amino acids, 5–10% carbohydrate, 3–5% lignin (Cowie and Hedges, 1992; Cowie *et al.*, 1992) and less than 5% total lipid (Tissot and Welte, 1978). As far as comparisons are warranted, it appears that the fractions of total organic matter in soils and coastal marine sediments that can be directly measured as carbohydrates, proteins, lignin and lipids are similar. More than two-thirds of the TOC in both soils and sediments typically cannot be accounted for at the molecular level, either because it is difficult to hydrolyze or has been degraded beyond chemical recognition.

Some examples of organic compounds which can serve as indicators of specific biological or geographic sources are given in Fig. 7. Most of the compound types are lipids, but biomarkers also occur among polar major biochemicals such as lignins (Hedges and Mann, 1979a) and cutins (Goñi and Hedges, 1990a,b). Distinctions between archaebacteria (methanogens, halophiles and thermoacidophiles), procaryotes (bacteria, cyanobacteria and photosynthetic sulfur bacteria) and eucaryotes (all other organisms including fungi, algae, and vascular plants) are possible, as well as among many common representatives of all three kingdoms. A particularly helpful tool has been the application of fatty acids derived from polar lipids (phospholipids and lipopolysaccharides) to estimate the types and amounts of microorganisms in natural samples (White, 1983, 1993; Mancuso *et al.*, 1990). This method, which has also been applied to agricultural soil (Zelles *et al.*, 1995) and rhizosphere samples (Tunlid *et al.*, 1985), is based on the observation that polar lipids degrade rapidly once a microorganism dies and thus primarily reflect living biomass. Biomarker-source relationships also can be used to infer previous environmental conditions or transport directions if the organism making the tracer is specific to a particular environment (Fig. 7) such as land (vascular plants), hypersaline water (halophilic bacteria) or anoxic conditions (sulfate-reducing and methane-forming bacteria).

Polar biochemicals such as carbohydrates and amino acids are broadly distributed, but often occur in abundance patterns that are characteristic of different sources. Thus, compositional differences among aldoses can be used to distinguish terrestrial versus marine organic sources, as well as angiosperms from gymnosperms, and bacteria from other organisms (Cowie and Hedges, 1984). *O*-Methyl sugars (Klok *et al.*, 1984), cyclitols (Anderson, 1972; Hedges and Weliky, 1989), and uronic acids (Bergamaschi, 1995) also occur in characteristic patterns among different organisms. Although protein amino acids are produced in nearly identical compositions by living organisms (Cowie and Hedges, 1992), muramic acid, diaminopimelic acid and the D-enantiomers of alanine and aspartic acid indicate mureins (peptidoglycans) from eubacterial cell walls (de Leeuw and Largeau, 1993). Many of the above publications include taxonomically-based surveys of potential sources that should be useful for soil studies as well.

Some organic compounds are also indicative of specific events or environmental transformations. Thus, the extent of degradation that an organic mixture has undergone can often be judged from such biochemically-based parameters as the percentage of total nitrogen in amino acid, the percentage of TOC in amino acids plus aldoses, or the percentage of nonprotein amino acid within the total amino acid hydrolysate (Fig. 8; Cowie and Hedges, 1992). Elevated vanillic acid/vanillin ratios are indicative of lignin degradation by fungi (Ertel *et al.*, 1986; Hedges *et al.*, 1988). Decreased percentages of

Fig. 7. Some examples of biomarker/source relationships among molecules of different chemical classes. References cited by number are: (1) Brassell and Eglinton, 1983; (2) Volkman *et al.*, 1980; (3) McCrindle and Overton, 1969; (4) Harrington *et al.*, 1970; (5) Kaneda, 1991; (6) Cranwell, 1981; (7) Brassell and Eglinton, 1984; (8) Goñi and Hedges, 1990a; (9) Volkman, 1986; (10) Morris and Brassell, 1988; (11) Ourisson *et al.*, 1987; (12) Wakeham *et al.*, 1980; (13) Perry *et al.*, 1979; (14) Fredrickson *et al.*, 1986; (15) Guckert *et al.*, 1985; (16) Poirier *et al.*, 1992; (17) Brassell, 1993; (18) De Rosa *et al.*, 1986; (19) Prahl and Pinto, 1987; (20) Parsons *et al.*, 1979; Rowan, 1989; (21) Stauber and Jeffrey, 1988; (22) Rabinowitch and Govindjee, 1969; (23) Repeta, 1993; and (24) Hedges and Mann, 1979a.
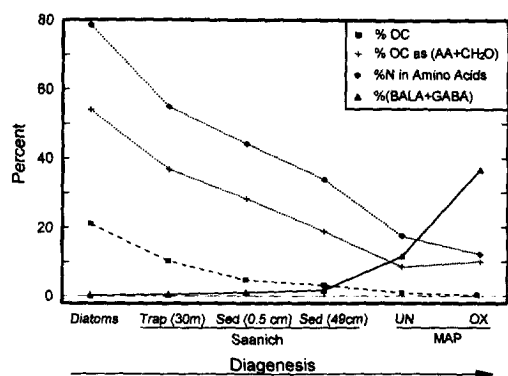
Fig. 8. Trends in biochemical indicators of diagenetic alteration in natural organic mixtures (from Cowie and Hedges, 1994).

glucose, sometimes accompanied by disproportionately large increases in rhamnose and fucose, are often observed during biodegradation in aquatic (Hedges et al., 1994; Hernes et al., 1996) and soil environments (Guggenberger et al., 1994a). Transitions along these alteration pathways can sometimes be traced to events such as the conversion of chlorophylls to phaeopigments in animal guts (Downs and Lorenzen, 1985), or to environmental conditions such as temperatures (Brassell, 1993; Simoneit, 1993).

CP/MAS $^{13}$C NMR detects almost all major organic carbon forms, providing an independent check on direct biochemical measurements. The main disadvantage of this method for mineral deposits is interferences by iron and other paramagnetic metals. The resulting decrease in spectral resolution and sensitivity has confined applications primarily to organic-rich samples. In the last decade it has become increasingly feasible, however, by treatments with dithionite and/or aqueous HF, to minimize paramagnetic interferences (e.g. Arshad et al., 1988; Preston et al., 1989a; Schmidt et al., submitted—b). For example, treatment of surface soils with 2% HF removes 80–95% of total Fe, while only 8–17% of TOC is lost with minimal compositional effects (Skjemstad et al., 1994b). As a result of such advances, NMR spectra for total organic matter in bulk soils and component size fractions are being published in increasing numbers (e.g. Kögel-Knabner and Ziegler, 1993; Preston et al., 1994; Guggenberger et al., 1995).

A CP/MAS $^{13}$C NMR spectrum of total organic matter in an HF-treated sample of a whole surface soil (Wiesenboden black earth) is presented in Fig. 9A. This clay-rich sample is representative of many A-horizon soils for which biochemical compilations have been determined (e.g. Skjemstad et al., 1994b). The spectrum exhibits strong resonances for carbons in alkyl (10–48 ppm), methoxyl (48–62 ppm); O-alkyl and di-O-alkyl (62–110 ppm), aromatic (110–160 ppm) and carboxyl (160–190 ppm)

structures. The percentages of alkyl carbon measured by NMR in such spectra are up to five-fold higher than concentrations cited for solvent-extractable lipid material (Stevenson, 1994), possibly due to the presence of cutin and suberin residues (Kögel-Knabner et al., 1992; Riederer et al., 1993). In general, fractions of carbohydrate-like carbon indicated by NMR analyses of soils (Oades et al., 1987) and peats (Preston et al., 1989b) substantially exceed sums of sugars detected by wet chemical methods. A complication in comparing $^{13}$C NMR and molecular data, however, is that individual NMR resonances often cannot be assigned unambiguously to a single biochemical source.

Corresponding spectra of whole marine sediments are rare, in part due to less experimentation with paramagnetic metal removal. Marine sediments accumulating in productive coastal regions away from strong river discharges, however, are often composed predominantly of opal or carbonate and thus include little interfering iron. To demonstrate the potential of this sample type for routine analysis, the CP/MAS $^{13}$C NMR spectrum of an untreated surface sediment (8.4 wt% OC) from the Peru Margin (Bergamaschi et al., 1997) is illustrated in Fig. 9B. Alkyl resonances comprise about half of the total resonance. Carbohydrate, aromatic and carboxyl structures account for comparable amounts of the remaining carbon. A similar alkyl-rich spectrum was published for bacterial material cultured from soils by Baldock et al. (1990), who noted that both fresh algae and fungi have dissimilar spectra characterized by strong carbohydrate resonances. The total aldose yield from the Peru sediment (Bergamaschi et al., 1997) corresponds to only about 15% of the apparent carbohydrate indicated by NMR (Fig. 9B) and in this characteristic resembles most soils.

Humic substances were first studied in terrestrial settings and are still the most commonly extracted and characterized fractions of soil organic matter (e.g. MacCarthy et al., 1990; Senesi and Miano, 1994). Conceptually, humic substances can be described as chemically complex, non-biochemical organic components; which are amorphous, dark colored, largely hydrophilic, and resistant to chemical and biological degradation (Schnitzer, 1991). In practice, humic substances are operationally defined on the basis of their water solubility at different pHs and are never free of biochemicals. The three fundamental types of soil humic substances are humin, humic acid and fulvic acid. A typical scheme for separating humic fractions is illustrated in Fig. 10. After removal of recognizable plant debris, the remaining humus is extracted exhaustively with dilute base (typically 0.1 N NaOH). Humin is the component of humus not soluble in aqueous base. The total base extract is acidified to a pH near 2 to precipitate the humic acid fraction. The
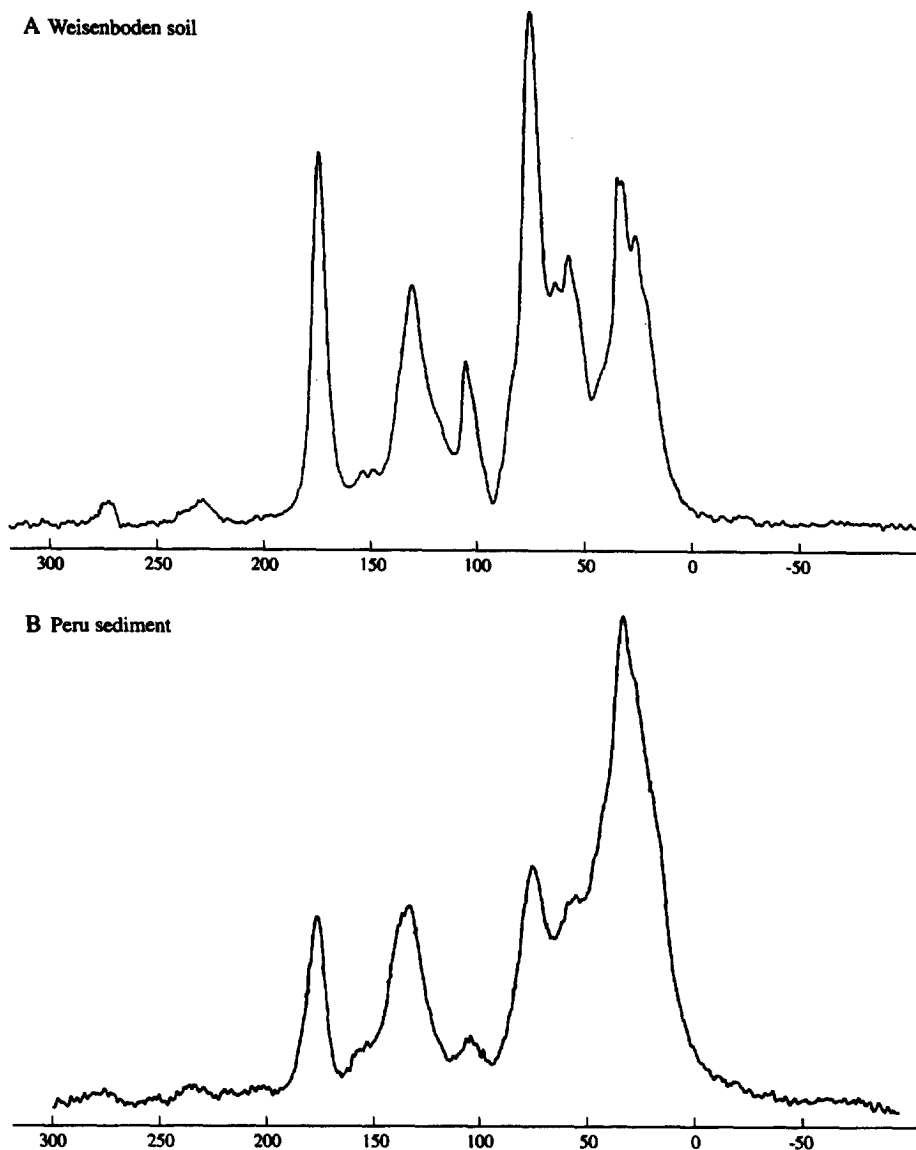
A Weisenboden soil



B Peru sediment

Fig. 9. CP/MAS $^{13}$C NMR spectrum of (A) organic matter in an HF-treated whole soil (Wiesenboden, Claremont) from near Adelaide, Australia and (B) an untreated whole sediment sample from the Peru margin (Bergamaschi et al., 1997).

material remaining in acid solution is fulvic acid. Relative amounts of different carbon types measured by CP/MAS $^{13}$C NMR in humic isolates from forest soils are illustrated in Fig. 11.

The relative amounts of the three humic fractions recovered from different soils vary widely. Although appreciable amounts of all three forms typically occur (Kononova, 1966; Schlesinger, 1991), fulvic acid is usually recovered in higher yields from acidic soils and from B versus A mineral soil horizons (Oades, 1978). In general, weight percentages of oxygen and cation exchange capacities increase from humin to humic acid to fulvic acid (Fig. 10),

due largely to increasing carboxyl content of progressively smaller molecules. Fulvic acids also are enriched in O-alkyl carbon, which contributes toward their characteristically high oxygen, and commensurably low carbon and nitrogen contents. The high average H/C (~1.5) of soil fulvic acid (Schnitzer, 1978) indicates an aliphatic nature.

Humic acids are commonly characterized humus fractions because these precipitates can readily be isolated in large amounts that are almost free of interfering inorganic matter. Soil humic acids typically show low H/C ratios near 1 (Schnitzer, 1978), consistent with a higher aromatic component than
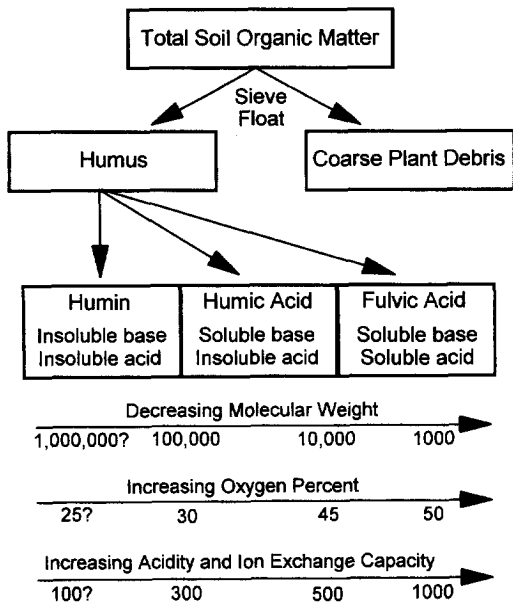
Fig. 10. Chemical fractions of soil organic matter with typical compositional characteristics of the humic fractions (after Oades, 1989).

half-life of small biochemicals during microbial degradation (Hatcher and Spiker, 1988). An additional complication is that some of the contrasting characteristics may result from direct extraction of biochemicals from vascular plant debris (e.g. Stevenson, 1994; Preston et al., 1994). For example, hemicellulose and pectin are soluble both in base and acid (Sjöström, 1981) and may contribute selectively to carbohydrate in fulvic acids (Ertel and Hedges, 1985). Cellulose is resistant to hydrolysis and likely augments the large $O$-alkyl component (Fig. 11) of humin fractions from soils containing abundant plant debris. When the humic fractionation scheme is applied to fresh bark and tree leaves, 10–25% of total tissue carbon is recovered as humic acid and 2–4 times as much as fulvic acids (Ertel and Hedges, 1985). The recovered humic acids are particularly enriched in lignin-derived phenols and other aromatic substances (Ertel and Hedges, 1985), as are soil counterparts
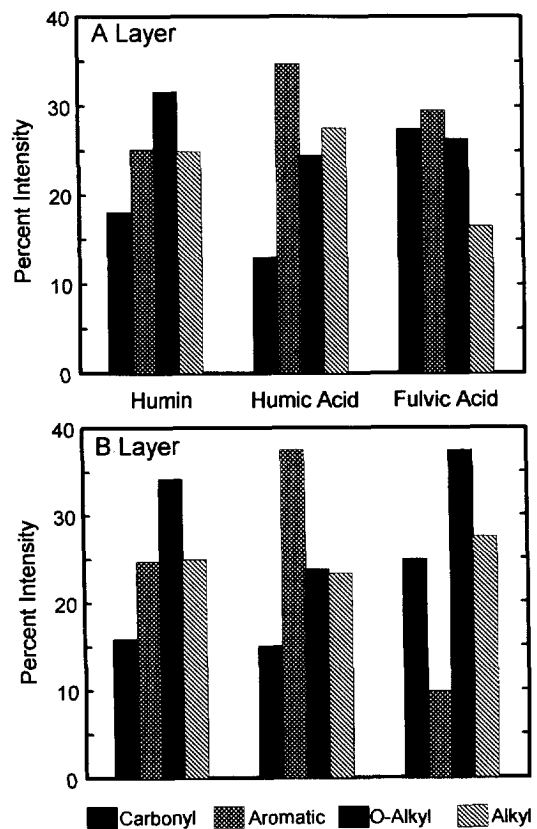
in corresponding fulvic acids. Degradative analyses of humic acids yield a wide variety of aromatic products including methoxylated phenols derived from lignin (e.g. Kögel, 1986; Schnitzer, 1991). Based on $^{13}$C NMR, Schnitzer (1991) estimated that 20–60% of the total carbon in soil humic acids is aromatic. The remaining aliphatic carbon occurs largely in alkyl chains and carbohydrate (Preston and Ripmeester, 1982; Fründ et al., 1989; Golchin et al., 1994a).

Humin is the least studied humic fraction because it is difficult to separate from the mineral matrix. The humin fractions in Fig. 11 were treated with HCl/HF and then physically concentrated after drying to minimize mineral interference. The resulting spectra show a predominance of $O$-alkyl carbon and are intermediate between fulvic and humic acid in acidic and aromatic carbon percentages. The features of high $O$-alkyl carbon and moderate acidity are similar to those obtained for local plant litter (Preston et al., 1994). Details about the spectral properties, degradation products and environmental dynamics of humic substances can be found in numerous reviews (e.g. Schnitzer, 1978; Stevenson, 1985; Frimmel and Christman, 1988).

It is clear from many studies that the three humic fractions are arbitrary subsets of a complex mixture of molecule types exhibiting a continuum of physicochemical properties. Interpreting the mechanisms that lead to these contrasting compositions is difficult. The classical model of step-wise biomacromolecule decomposition to small intermediates which subsequently condense to form geomacromolecules (Tissot and Welte, 1978) is unlikely due to the short



Fig. 11. Percentage intensities of group resonances obtained by CP/MAS $^{13}$C NMR of humin (solid-state), humic acid (in solution) and fulvic acid (in solution) fractions recovered from the A (7–13 cm) and B (18–30 cm) layers of a soil profile under a young Douglas-fir stand in coastal British Columbia, Canada (data from Preston et al., 1994). The illustrated alkyl, $O$-alkyl, aromatic and carbonyl carbon percentages correspond to the summed relative intensities in their Table 5 for the 0–48, 48–110, 110–160, and 160–210 ppm resonances, respectively.

(Guggenberger *et al.*, 1995; Knicker and Lüdemann, 1995; Fig. 11). Partial degradation of plant tissues in sediments and soils substantially increases base solubility and thus humic and fulvic acid yields (Hedges, 1990; Kögel-Knabner and Ziegler, 1993; Golchin *et al.*, 1994a). Although humic fractions reflect properties of the parent soil organic mixture, many of the variations *among* humic fractions appear to be induced by harsh (pH 13-2) chemical fractionations (Fig. 10) which have no natural analog (Oades and Ladd, 1977).

Humic substances have not been so broadly studied in sediments. The long-held notion that marine humic substances are the main progenitors of highly aliphatic kerogens characteristic of marine source rocks (Tissot and Welte, 1978; Durand, 1980), however, has engendered some research. Marine sediments also provide the opportunity to follow slow organic interconversions in long depositional sequences, and to test specifically for humic substance formation from largely aliphatic precursors. When isolated by the same procedures used for soils, sedimentary humic substances are recovered in comparable yields. Total base extractable carbon is typically in the range of 25–50% of TOC, and humic/fulvic acid ratios vary widely (Stuermer *et al.*, 1978; Rashid, 1985). The elemental compositions, acidities, molecular weights and other bulk properties of individual sedimentary humic fractions (Rashid, 1985) follow similar internal trends as seen for soils (Fig. 10). As a group, however, sedimentary humic substances exhibit distinct compositional characteristics which result from a predominantly plankton, rather than higher plant, origin. These inherited properties include lower C/N, more positive $\delta^{13}C$ values, higher H/C, sparse lignin, and a lower total aromatic carbon content (Stuermer *et al.*, 1978; Hatcher *et al.*, 1983a).

Increasing ratios of humic acid to fulvic acid, and of humin to humic acid, at greater depths in marine sediment cores (e.g. Brown *et al.*, 1972) have been interpreted to represent progressive *in situ* condensation of reactive small molecules to yield increasingly larger "heteropolycondensates", including insoluble "proto-kerogen". However, proto-kerogen, like humin, is also found at high concentrations in young samples (Stuermer *et al.*, 1978). Increasing realization that vascular plants, algae and bacteria all produce hydrolysis-resistant biomacromolecules that are highly resistant to biodegradation and operationally identical to kerogens (Tegelaar *et al.*, 1989; de Leeuw and Largeau, 1993) has called into question the whole concept of spontaneous condensation reactions attending diagenetic alteration (Hatcher *et al.*, 1983b; Hatcher and Spiker, 1988). Even under conditions of extensive degradation within well defined systems such as vascular plant fragments, convincing evidence has not been presented for appreciable formation of structu-

rally complex nonbiochemical products indicative of "humification reactions" (Hedges *et al.*, 1985; Knicker *et al.*, 1993; Knicker and Lüdemann, 1995). A number of kerogens in ancient rock have now been shown morphologically and chemically to resemble the cuticles and cell walls of ancient plants and microorganisms (Goth *et al.*, 1988; Nip *et al.*, 1989). Although interest in marine humic substances as precursors of kerogens and petroleums has waned, condensation reactions may still occur, especially natural volcanization (Kohnen *et al.*, 1989) and among organic molecules concentrated on mineral surfaces (Collins *et al.*, 1995).

### Physical separations

Fractionations based on particle size and/or density are being used increasingly as alternatives to chemical techniques (e.g. base extraction) for concentrating and characterizing organic matter from soils. Such separations are chemically mild and more closely parallel natural sorting of particles during transport by water and wind (Keil *et al.*, 1994c). Textural fractionations are usually done by dispersing soil with shaking or ultrasonic treatment, after which released particles are separated by wet sieving and/or gravity sedimentation (Christensen, 1992; Christensen, 1996). Densimetric fractionations usually involve floating light organic particles in heavy liquids having densities from 1.5–2.5. Physical separations have the advantage that they provide important information about the forms and physical environments of organic materials, with less potential for chemical artifacts than with drastic chemical treatments.

In essentially every case where soils have been texturally separated and the elemental composition of the fractions analyzed (e.g. Monrozier *et al.*, 1991; Guggenberger *et al.*, 1994a), a trend toward lower C/N in finer size particles has been observed (Christensen, 1996). This pattern is evident from a plot (Fig. 12A) of C/N for the previously discussed size fractions from soils studied by Turchenek and Oades (1979). In all four soils C/N decreases from values near 20 for sands to minimal ratios of 7–9 in medium clay. Microscopic observation, density separations and chemical analyses all indicate that high concentrations of coarse vascular plant debris in various stages of degradation are responsible for elevated C/N ratios in coarse sands (Christensen, 1996). The low C/N of finer soil particles appears to result primarily from selective concentration of nitrogenous organic substances, as opposed to ammonium (Christensen, 1996).

Amino acids, including bacterially-derived diaminopimelic acid, also are recovered in elevated yields from clay and silt fractions of most soils (Christensen, 1996), where they compose high percentages of total nitrogen (Christensen and Bech-Andersen, 1989). Sørensen (1983) noted that when
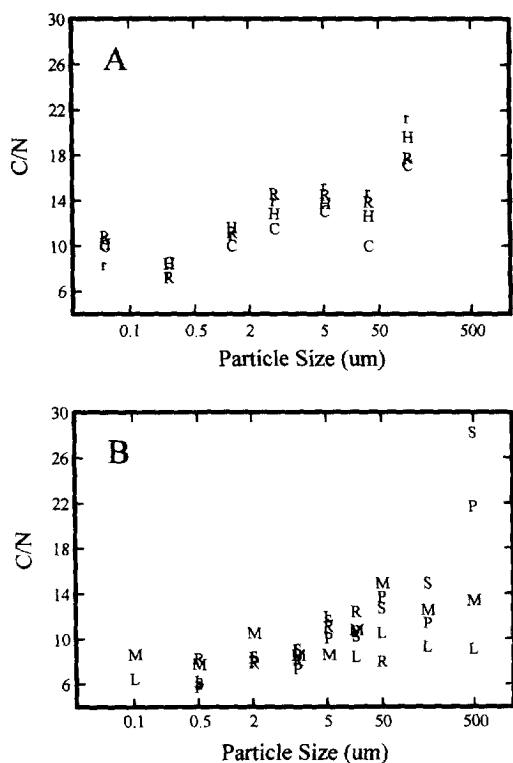
Fig. 12. Comparative plots of C/N versus mean diameter (μm) for particle size fractions from (A) soils (Turchenek and Oades, 1979) and (B) coastal marine sediments (Keil *et al.*, 1994c). Symbols for the soil samples are Haploboroll (H), Calciaquoll (C) and Rhodoxeralf types, the latter in permanent pasture (R) and wheat/fallow (r) rotation. Sediment symbols are plume (P), shelf (S), O₂ minimum (M) and slope (L).

$^{14}$C-labeled cellulose was introduced to soil, about half of the radiocarbon remaining after one year of incubation was recovered in amino acids. Less than 40% of the total remaining nitrogen, however, occurred in amino acid, versus values near 60% for living organisms (Cowie and Hedges, 1994). Even at the high end of their abundance range, living microorganisms are unlikely to account for more than 10% of total soil nitrogen. Microorganisms thus appear to contribute to soil nitrogen indirectly, by biosynthesizing proteins, chitin and other nitrogen-rich organic matter, whose residues apparently are released to the soil by degradation and protected from complete mineralization by association with silt- and clay-size particles.

Other biochemical trends occur across the size spectrum of particles separated from soils (Christensen, 1996). Ratios of (galactose + mannose)/(arabinose + xylose) and of (rhamnose + fucose)/(arabinose + xylose) increase from sand to silt to clay (Turchenek and Oades, 1979; Guggenberger *et al.*, 1994a), indicating higher fractions of microbial polysaccharides in finer size fractions. Carbon-normalized yields of lignin phenols

derived from CuO oxidation of bulk organic matter in A-horizons of different soils (Guggenberger *et al.*, 1994a) consistently decrease with grain size (Fig. 13A). This drop is accompanied by steady elevation in the weight ratio of vanillic acid/vanillin from values in sands near 0.2, characteristic of fresh vascular plant tissues, to ratios in clays of up to 1.0 (Fig. 13A), indicative of extensive fungal degradation (Goñi *et al.*, 1993; Nelson *et al.*, 1995). Lignin in the sand-size fraction appears to be in slightly modified vascular plant debris, whereas lignin residues in clays are highly degraded (Guggenberger *et al.*, 1994a).

CP/MAS $^{13}$C NMR analysis gives a broad view of organic compositional trends with size and density (e.g. Oades *et al.*, 1987; Baldock *et al.*, 1991). Averaged results of a study (Baldock *et al.*, 1992) where five size fractions were separated from four well-dispersed soils prior to densimetric fraction and NMR analysis are illustrated in Fig. 14. In general, O-alkyl resonances of carbohydrate-like materials predominate across the entire textural range, but minimize in the silt fraction. The strongest O-alkyl signal is in sands where >75% of TOC is plant debris. Aromatic carbon resonances maximize within silts and are lowest in the two clay fractions
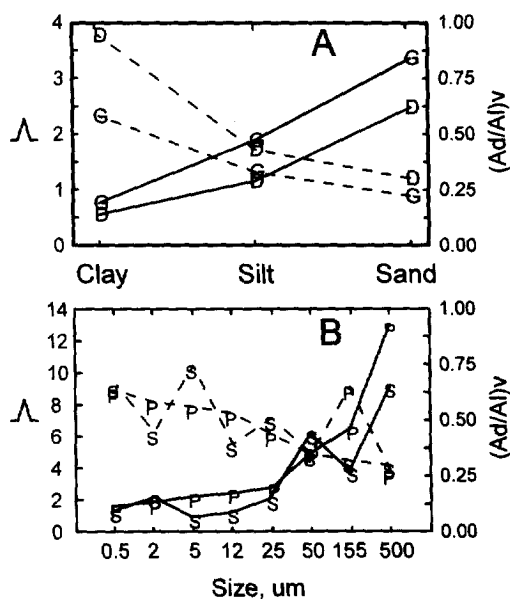


Fig. 13. Yields of total lignin-derived phenols, Λ, per 100 mg OC, as well as vanillic acid/vanillin ratios, (Ad/Al)v, obtained by CuO oxidation of size fractions from (A) the A horizons of two Bavarian soils (data from Guggenberger *et al.*, 1994a) and (B) two surface marine sediments from the Washington state, USA, coast (data from Keil *et al.*, 1994c). In both plots, solid lines symbolize Λ and dashed lines indicate (Ad/Al)v. Results for soils from mixed deciduous forest and permanent grassland are represented in (A) by D and G, respectively. Sediments from the plume and continental slope are indicated in (B) by P and S, respectively.
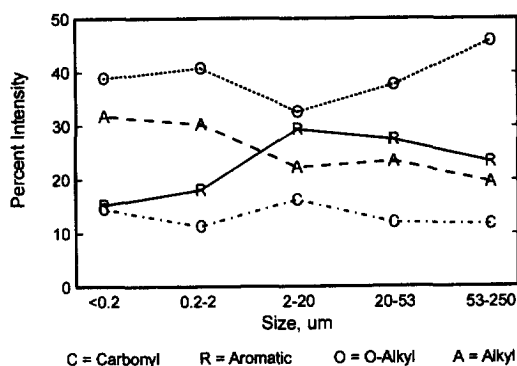
Fig. 14. Average percentage intensities of group resonances obtained by CP/MAS $^{13}$C NMR for size fractions of two Mollisols and two Oxisols (Baldock *et al.*, 1992). The two < 0.2–2.0 μm size fractions were analyzed whole, whereas the three 2–250 μm samples were > 2.0 g/cm$^3$ density separates. Resonance designations are as in Fig. 11.

which contain over half of the TOC. Alkyl carbon increases with decreasing size to become the second-most abundant component in the clay isolates. Carboxyl groups account for 10–15% of total carbon across all size fractions. Similar patterns have been observed for size isolates of a mineral soil (Oades *et al.*, 1987) and peat (Preston *et al.*, 1989b).

Baldock *et al.* (1992) have ascribed these textural differences to two simultaneous processes whose net effects vary with particle size. The first mechanism is physical and chemical breakdown of coarse vascular plant fragments within the sand fraction, attended by selective loss of carbohydrate. The resulting lignin-rich debris contributes to the aromatic carbon maximum in the silt fraction. Selective lignin degradation and size reduction continue, yielding a remnant of highly altered aromatic material intimately associated with clay-size minerals (e.g. Figure 13A). The second process is accumulation of nitrogen as polysaccharides and lignins from vascular plant tissues are sequentially converted via microbial biomass to residual "metabolites". C/N progressively decreases from values of 20–400 for fresh vascular plant tissues, to ratios of 15–45 for sand-size plant debris, 13–25 for particles < 2.0 g/cm$^3$ in silt, and 7–15 for bulk clay-size material (Baldock *et al.*, 1992). The sharp decrease in aromatic carbon from silt to clay, and corresponding increases in alkyl and O-alkyl carbon (Fig. 14) indicate that the nitrogen-rich organic matter preferentially associated with finer mineral material is highly aliphatic and includes appreciable polysaccharide. In a separate experiment where soil was size fractionated after being inoculated with $^{13}$C-labeled glucose, Baldock *et al.* (1990) demonstrated that most of the label is incorporated into O-alkyl and alkyl carbon associated with clay-size particles.

These previous indications that aliphatic, nitrogen-rich microbial remains make up much of the

organic matter persisting with fine minerals in soils have been recently supported by CP/MAS $^{15}$N-based studies. Knicker *et al.* (1993) demonstrated by applying this technique to bulk native soils and their humic fractions that approximately 85% of the total nitrogen signal from all samples derives from amide/peptide structures, with almost all the rest coming from various amino groups. No evidence was found for appreciable amounts of nitrogen in heterocyclic substances or Schiff bases which should be indicative of humic substances derived from spontaneous condensation reactions (Hedges, 1988). Similar results were obtained in a laboratory culturing experiment (Knicker and Lüdemann, 1995) where double-labeled ($^{15}$N and $^{13}$C) wheat was composted under aerobic conditions for almost 2 years. This evidence for a major protein-like component was supported by strong direct correlations between the nitrogen contents of the degrading tissues and their carboxyl and alkyl carbon intensities measured by $^{13}$C NMR.

Physical separations of sediment particles have been relatively rare and generally have involved either picking (Hedges and Weliky, 1989; Goñi and Hedges, 1990b; Benner *et al.*, 1990a,b) or floating small plant debris with liquids (Prahl and Carpenter, 1983; Ertel and Hedges, 1985). In such comparisons the C/N of the remaining debris decreases (Hedges *et al.*, 1985; Opsahl and Benner, 1995). Of the few studies where bulk sediments were size fractionated and analyzed for biochemicals, Thompson and Eglinton (1978) found that clay fractions of lake sediments are enriched in microbial hydrocarbons and fatty acids, whereas long-chain lipids from vascular plant debris are concentrated in larger size fractions. Tanoue and Handa (1979) observed evidence for selective uptake of amino acids by silts. In studies of hydrodynamically-separated sedimentary material from the Washington State continental margin, Keil *et al.* (1994c) found a progressive decrease in C/N with smaller particle size (Fig. 12B), similar to that observed for soils (Fig. 12A). A plot of C/N versus $\delta^{13}$C for the sediment size fractions (Fig. 15) indicates mixing of isotopically light, nitrogen-poor vascular plant debris in the silt and sand fractions with more $^{13}$C- and nitrogen-rich organic matter of marine origin. An additional trend, only expressed by clay size fractions, corresponds to mixing of marine plankton remains with isotopically light soil organic matter (C/N = 8–14). Patterns of lignin phenol yield and acid/aldehyde ratios (Fig. 13B) across size fractions of these sediments (Keil *et al.*, submitted) resemble those of forest soils (Fig. 13A). These similarities indicate that many chemical relationships imprinted into the particulate matrix of soils are retained during transport to coastal marine sites and subsequent accumulation. Terrigenous organic matter, and the mechanisms of its association with
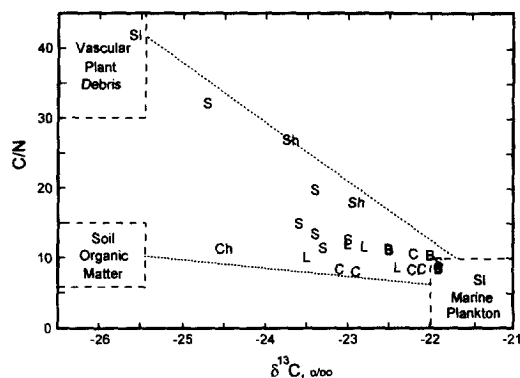
Fig. 15. Trends in atomic C/N versus $\delta^{13}C$ for sand (S), silt (L) and clay-size (C) sedimentary particles collected from the Washington State continental shelf and slope. The subscript "h" indicates heavy particles and "l" indicates light particles floated with heavy liquids. Data are from Keil et al. (1994c).

soil minerals, are evident in coastal marine sediments in spite of extensive transport and storage.

## Dynamics

The turnover of organic matter in different soils has been an important subject in both agronomic and environmental studies (Christensen, 1996). Dynamic data have been obtained primarily by following the fates of different $^{14}C$-, $^{13}C$- or $^{15}N$-labeled materials in natural environments and laboratory plots. In general, turnover of organic matter increases with decreasing particle size (Christensen, 1996). Isotopically labeled C and N accumulates selectively in clay-size material, either rapidly when dissolved substrates are added, or over time when plant tissues are degraded (Christensen and Sørensen, 1985; Magid et al., 1996). It seems contradictory that carbon turnover would be highest in the same clay fractions that preserve the highest weight percentages of OC. These observations are not exclusive, however, if dissolved substrates are shunted primarily through biologically active clay fractions which simultaneously maintain a large pool of organic matter (Nelson et al., 1994). The ability of clays to stabilize organic matter also is indicated by enhanced retention of labeled organic matter after addition of clay minerals to sandy soils (Ladd et al., 1985). Dissolved organic substrates appear to pass first via porewater to clay size fractions where microbial biomass is concentrated (Gregorich et al., 1991; Christensen, 1996), and eventually to larger size fractions if the clays aggregate.

How is a major portion of soil organic matter preserved in metabolically-active fine clay fractions? The previous compositional information suggests, since living biomass is so small (~3% of TOC), that most remnant organic matter is retained as nonliving microbial remains. To resist rapid removal by

percolating water, and sink in densimetric isolations, this organic material must be associated strongly with fine minerals (Christensen, 1992). The observation by Skjemstad et al. (1993), that one-quarter to one-third of organic matter in silt- and clay-sized aggregates is resistant to high energy UV photodegradation, suggests that this fraction occupies a protected internal location. Loadings of OC per unit surface area onto finer soil particles (Fig. 6) are near values expected for a single-layer organic coating. Because most of the volume and surface area of soils are in pores smaller than bacteria and their exoenzymes, surface association should be protective toward microbial degradation (Adu and Oades, 1978). Microbial cell walls and mucilages (glycocalyx) must adhere strongly to mineral grains (Foster, 1988). Microbial metabolites in particular are rich in positively charged nitrogenous compounds whose sorption onto negatively-charged clay mineral surfaces is electrostatically favored (Theng, 1974; Hedges, 1978; Hedges et al., 1994). Protective sorption would also help explain the rapid biodegradation of DOC once dissolved from soil minerals (Nelson et al., 1994) and the apparent inconsistency between essentially complete degradation of chemically recognizable lignin in the same soils where seemingly labile organic matter rich in nitrogen, alkyl carbon and polysaccharide accumulates.

Fire is unique to terrestrial settings and may have a profound influence on the compositions and dynamics of soil and sedimentary organic matter. Kuhlbusch and Crutzen (1995) estimated that approximately 0.05–0.3 Gt/yr of "black carbon" are now produced globally by fires, most of which are started by man. Black carbon is defined by the authors as finely-divided, highly aromatic (H/C ≤ 0.2) graphitic material, that is resistant to oxidation in pure $O_2$ at 340°C. Black carbon represents only the most carbon-rich component of all charred materials (including charcoal) produced by high temperature burning and is one of the most resistant forms of reduced carbon toward chemical oxidation (Wolbach and Anders, 1989; Gustafsson et al., 1997; Verardo, 1997). Black carbon and charcoal are often found in soils (Shindo, 1991; Skjemstad et al., 1996) and marine sediments (Griffin and Goldberg, 1975; Goldberg, 1985). The above conservatively estimated production rate of black carbon on land corresponds to 25–100% of the global rates at which POC is discharged by rivers to the ocean and buried in marine sediments (Fig. 1). If these modern day flux estimates are accurate, black carbon could now compose a major fraction of all organic carbon carried by rivers and buried in marine sediments. If not being mobilized off the continents at this high rate, black carbon must be either accumulating rapidly in soils and freshwater sediments, or extensively mineralized on

land by an extremely severe oxidative mechanism. Coals are degraded at outcrops (Nip et al., 1989) and even black carbon is reportedly oxidized by microorganisms in some soils (Shneour, 1966; Clarke et al., 1995). Because oxidation of black carbon should increase its acidity and base solubility, this reaction may explain the high aromatic content of humic substances extracted from soils subjected to continued burning (Kumada, 1983; Haumaier and Zech, 1995). Greater knowledge of the pathways and fates of black carbon is needed to better balance global cycles and understand mechanisms for mineralization of resistant organic materials of all types in soils and sediments.

Dynamics of organic materials have been extensively studied in marine sediments (Berner, 1980; Henrichs, 1992, 1993), in which vertical profiles of diagenetic reactants and products reflect reaction rates and stoichiometries (Berner, 1980). Measurements of $^{14}C$ and other radiochemicals provide the needed accumulation rate information. Fast reactions can also be followed by tracer injections (Henrichs, 1993) or by measuring fluxes of dissolved chemicals across the sediment/water interface (Devol, 1987). Calculated rate constants for organic matter mineralization in marine sediments vary by over a factor of a million from about 1-10 $-6\,yr^{-1}$ (Middelburg et al., 1993). Measurable degradation occurs on all time scales studied, resulting in a one-to-one relationship between the measured rate constant and the observation time span (Fig. 16). This close correspondence occurs because faster-reacting organic materials disappear at the start of the observation period (or top of a core section), whereas slower reacting components do not change measurably in concentration over the duration of the experiment (or core length). Similar temporal bias occurs in soil studies, making difficult meaningful comparisons of absolute rate constants between different physical environments and sample types. Patterns in the relative rates of reaction among different substrates, however, can be informative.

A few clear trends come out of kinetic studies of organic matter degradation in marine sediments (Henrichs, 1993). One is that sedimentary degradation rates increase with increasing input of sinking particulate material, and hence with local plankton productivity. This direct relationship is expected because only a small fraction of the depositing organic matter is eventually preserved (Fig. 1). A second common observation is that initial reaction rates of bulk organic matter and many of its major components are essentially the same under oxic and anoxic conditions (Henrichs, 1992, 1993). This generality holds for most oxygenated organic matter such as polysaccharides and proteins, but not for lignins and other carbon-rich polymers which are not as easily hydrolyzed and fermented
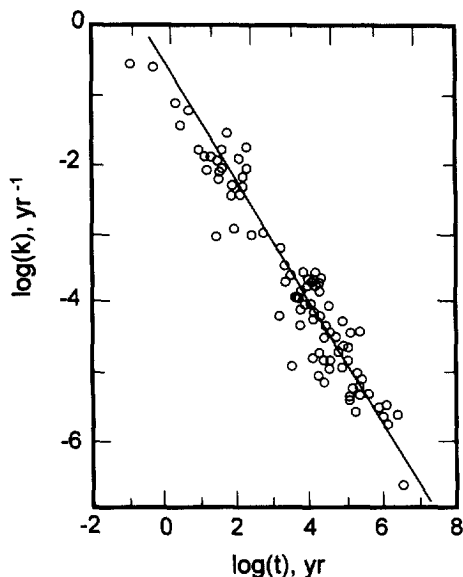


Fig. 16. Log/log plot of the measured reactivity ($k$) of OC versus the time interval ($t$) of experimental measurement. All data are for organic matter degradation within marine sediment cores (after Middelburg et al., 1993).

(Emerson and Hedges, 1988). Third, when not smeared by rapid bioturbation, concentration profiles for total sedimentary OC decrease exponentially with depth, but (a) at faster rates near the surface than expected for simple first-order decay and (b) to constant non-zero values at depth. Such behavior can be modeled by assuming either multiple components reacting at different rates (Westrich and Berner, 1984) or by assuming that the decay "constant" for total organic matter is itself a function of time (e.g. Middelburg, 1989; Boudreau and Ruddick, 1991). As with soils, sedimentary systems are usually modeled as containing two to three types of organic matter characterized by different first-order decay constants. These "multi-G" models are useful in describing the kinetics and stoichiometry of early mineralization, but not necessarily for understanding the extent of ultimate preservation of an organic remnant at depth (Cowie et al., 1995). In sediments, as with soils, the rates of initial degradation and extents of eventual organic preservation may be decoupled, and controlled by different mechanisms.

## COMMON CHALLENGES AND PROMISING RESEARCH AREAS

The distributions and dynamics of organic materials in soils and sediments are similar enough to allow meaningful comparisons, but sufficiently different to provide useful contrasts. Because coastal marine sediments often contain major components of soil-derived organic matter (e.g. Figure 15), information about organic matter distributions

and dynamics on land will also pertain to many coastal marine systems. In this section we will focus on outstanding examples of key research areas where potential exists for beneficial exchanges of information and techniques.

### Structural relationships in mineral-organic systems

The issue of how organic matter and mineral material are associated in soil and sedimentary mixtures is an outstanding example of an important problem area ripe for crosscutting studies. The scale of interactions between organic matter, microorganisms and inorganic materials has been a central theme in soil studies for decades (Oades, 1988, 1989), but only a sidelight for sediments. It is evident from the previous discussion that size- and density-based separations of particulate material in soils and coastal marine sediments resolve light, sand-size vascular plant debris from smaller, more nitrogen-rich microbial remains associated with minerals (Figs 13–15). A key question, however, for both systems is whether the commonly observed decrease of C/N in smaller silt and clay size fractions (Fig. 12) is due simply to decreasing relative concentrations of vascular plant fragments in smaller size fractions, or to increased association of nitrogen-rich molecules with finer mineral grains (Hedges and Keil, 1995). The latter possibility is suggested by parallel decreases of C/N with particle size for offshore marine sediments poor in vascular plant materials (Keil et al., 1994c) and for finer soil particles with increasingly lower lignin contents (Fig. 13). This problem could be addressed for soils by employing hydrodynamic particle fractionation techniques (Keil et al., 1994c) which allow close separations in the clay to silt range where mineralogy is most variable. Soils also provide the opportunity to collect a suite of samples with mechanistically informative contrasts in texture, mineralogy, and organic matter sources.

A related question is whether physical protection of organic particles occurs within mineral aggregates of marine sediments as has been found for soils (Tisdall and Oades, 1982; Golchin et al., 1994a). Although seawater may be too "sodic" for strong aggregation of clay-rich particles via divalent cation linkages, its high ionic strength causes extensive flocculation and binding of mineral grains by microbial or animal mucilages is common (Syvitski, 1991). In addition, compaction and cementation eventually lead to stronger particle associations in deeper sediments. Physical protection in mineral aggregates might help explain the high organic concentrations typical of marine sediments accumulating under $O_2$-poor ( $< 20 \mu M$) bottom waters, where animals that disrupt sediment fabrics are largely excluded. One way of testing for physical protection by particles might be to texturally separate marine sediments in seawater (versus distilled water) in an attempt to isolate intact aggregates for subsequent analysis. Alternatively, sediments could be physically disaggregated and monitored for accelerated microbial activity corresponding to increasing substrate exposure.

One of the biggest impediments to comprehensive studies of the above questions, and of the ultrastructures of soils and sediments in general, has been the difficulty of visualizing the dynamic and structurally intricate associations of mineral particles, living microorganisms, organic remains and water on the nanometer scale. The greatest strides in this research area have been for soils, and specifically in application of ultracytochemical "stains" of electron-dense elements prior to SEM and TEM analysis of largely intact particle assemblages (e.g. Foster, 1985, 1988). Conventional SEM/TEM studies, however, require painstaking sample preparation, including drying, physical stabilization in resin or gel, coating with a conductive film, and analysis under high vacuum. Such preparative treatments can distort the original associations of the diverse component particles, especially for ocean sediments in which salt crystals form upon drying. Environmental scanning electron microscopy (ESEM) is a developing technology that sidesteps many of these problems (Danilatos, 1991). ESEM tolerates moderate gas pressures (up to $\sim 5$ Torr) and thus accommodates the presence of liquid water in the specimen at room temperature. This capability allows examination of both conducting and nonconducting samples, in either wet or dry form, at the resolution of conventional SEM. ESEM is compatible with energy-dispersive X-ray microanalysis (Edgerton-Warburton et al., 1993) and thus has the additional capability of selectively detecting biopolymer-specific metal stains as have been used in ultracytochemical studies (Foster, 1985). ESEM has now been applied to a variety of sample types including environmental colloids, hydrocarbons in reservoir rocks and microorganisms (Griffith and Danilatos, 1993). This method thus should be applicable across a broad front in studies of ultrastructural relationships in soils (e.g. Ladd et al., 1996) and sediments. For example, the distributions of vascular plant debris could be determined in relationship to C/N and lignin trends across the textural spectrum (Figs 12 and 13). In addition, the spatial relationships of bacteria, substrates and mineral voids could be detailed with respect to mechanistic implications. If selective staining is possible without physical disruption of the sample, the important question of the distribution of organic materials on mineral surfaces and within pores could be addressed.

### Sorption-related processes

Almost all early research on sorption of organic substances onto minerals was for soils (e.g.

Greenland, 1965a,b) and "clean" laboratory systems (Weiss, 1969). Continued research (Theng, 1974, 1979) has shown that partitioning between dissolved molecules and mineral surfaces is only slowly reversed (Fusi et al., 1989; Gu et al., 1994) and highly selective for large organic molecules (Greenland, 1965a) that are hydrophobic (Dunnivant et al., 1992; Day et al., 1994) and nitrogen-rich (Ben-Hur et al., 1992; Letey, 1994). In contrast, recent research related to organic/mineral associations in soils has been increasingly aimed at establishing empirical relationships between organic storage and textural characteristics (e.g. Parton et al., 1993; Schimel et al., 1994; Powlson et al., 1996) or passage of dissolved organic materials through soil into groundwater and streams (e.g. Qualls and Haines, 1992; Nelson et al., 1993; Guggenberger et al., 1994b). The explanation usually given for the almost universal increase in % OC with decreasing particle size is better physical protection of organic particles within aggregates of smaller mineral grains (e.g. Parton et al., 1993), as opposed to stabilization by sorption onto mineral grain surfaces. However, the organic materials comprising the larger, less reactive pools in soils are nitrogen rich, intimately associated with minerals and vary directly in concentration with mineral surface area in a range whose lower limit is near that expected for a single coating of sorbed organic matter (Fig. 6). In addition, an appreciable component of soil organic matter can be desorbed by water, after which it is readily degraded by microorganisms (Smith et al., 1992; Nelson et al., 1994). These characteristics, and especially preferential retention of nitrogen-rich organic matter in soils, point toward sorption, rather than aggregation, as the main protective mechanism.

In contrast, recent evidence that most of the organic matter in continental margin sediments is associated with mineral surfaces (Mayer, 1994a,b; Keil et al., 1994c), and thereby physically-protected (Keil et al., 1994b), has made sorptive processes an area of active research in marine organic geochemistry (Lee, 1994). Related issues now being investigated include the distribution of organic matter on sedimentary mineral surfaces (Mayer, 1994a), reversibility of sorption (Wang and Lee, 1993), and the effects of competition between partitioning and degradation on the concentrations of the dissolved and sorbed organic fractions (Henrichs and Sugai, 1993; Henrichs, 1995). Surface areas are being increasingly measured because they can be readily determined and offer a more meaningful method than % OC for interpreting and comparing organic matter concentrations among mineral matrices. In particular, surface loadings substantially in excess of the average of 0.5–1.0 mg $OC/m^2$ appear to be a useful indicator of sediments rich in plant debris (Fig. 6) or depositing below low-$O_2$ bottom water.

Unusually low loadings, on the other hand, often correspond to high inputs of organic-poor mineral material such as loess (Keil et al., 1997) or extensive degradation, as is typical of open ocean sediments (Hedges and Keil, 1995). Given these promising developments for subaqueous systems and the general acknowledgment that sorption and aggregation are important protective processes on land (Theng, 1979; Oades, 1989), additional attention to the comparative measurement of surface areas in soils and aggregates in marine sediments seems warranted.

### Microbial metabolites

Studies of the breakdown of organic matter are particularly advanced for soil systems, where the sizes and biochemical compositions of the predominant vascular plant producers and microbial degraders are so recognizably different. This contrast has revealed that vascular plant tissues rich in tannin and lignin are almost completely destroyed, whereas acidic, nitrogen-rich aliphatic material persists in strong association with mineral grains (Fig. 14). Given the immense mass of organic matter stored in surface soils (Fig. 1) and its preferential association with clays, this nitrogenous material is one of the most abundant forms of reduced carbon on earth. Although it usually has been assumed that mineral-associated soil organic matter represents the "humified" remnants of degraded vascular plant tissues spontaneously combined with smaller amounts of microbially-derived remains, it seems more likely based on recent evidence (e.g. Baldock et al., 1992; Knicker et al., 1993) that microbial products actually predominate. The comparably high concentrations of humic substances and adsorbed organic matter in most soils and sediments suggest that major fractions of both operationally-defined materials may be one and the same. How these materials form and become associated with surfaces is unknown, as are the consequences of these processes.

The nature of "microbial metabolites" is among the most important questions in organic geochemistry today. Are they microbial mucilages, fragments of cell walls still attached to mineral surfaces; or simply a hodgepodge of molecules which have competed successfully for mineral surfaces? Why are biochemical yields so low versus concentrations indicated by spectroscopic techniques? One possibility is that a specific class of microbial biomacromolecules might persist that is both resistant to degradation and has a high affinity for mineral surfaces. A possible example of such materials could be the non-hydrolyzable, amide-containing macromolecule recently discovered in the cell walls of green microalgae (Derenne et al., 1993). Such substances could be selectively preserved in soils and missed because they are not easily detected by conventional analytical means (Oades, 1995). Rigorous

combinations of bulk chemical and molecular-level analyses will be needed to attack this key problem. In particular, suites of biomarkers specific for microbial sources should be applied in tandem with comprehensive methods such as $^{15}$N NMR to simple systems where well-defined plant materials are degraded by known microorganisms (e.g. Knicker and Lüdemann, 1995).

### Oxic degradation

One striking aspect of the OC cycle is that lignins, tannins, humus, and even kerogen must be almost completely degraded in the environment, leaving only one in 500 biosynthesized organic carbons ultimately preserved in marine sediments (Fig. 1). Extensive mineralization of these carbon-rich, structurally complex macromolecules requires extremely severe and nonspecific oxidation as has been observed in deep-sea turbidites. Mineralization might involve either $O_2$ directly or redox couples of metal ions, Fe(III)–Fe(II) or Mn(IV)–Mn(II), acting as intermediate electron transfer agents (Hedges and Keil, 1995). Such reactions could be either biologically mediated or spontaneous and may be so slow that conventional laboratory simulations would be difficult. Because soils are generally oxic, the organic matter they contain almost certainly is subject to similarly severe degradation processes, although masked by continuous input of fresh organic matter. Degradation of pollen in soils, for example, is well known (Elsik, 1971) and mass balance suggests that even charcoal may be appreciably mineralized (previous discussion).

The opportunity for comparative research of oxic degradation in soils and sediments is great. Marine turbidites offer extreme "before and after" examples of the effects of *in situ* oxidation, but afford limited spatial resolution within their usually sharp redox gradients. Soils, in contrast, may function more as stirred batch reactors within which discrete particles such as pollen grains or charcoal fragments may exhibit a whole range of effects of oxic degradation, although possibly to a greater extent deeper in the profile. Soil samples are easily recovered, have well defined environmental characteristics and histories, and could be chosen to allow the study of selected substrates such as kerogen or coal derived from weathering bedrocks. Comparisons between soils and sediments could also be mechanistically informative due to differences in predominant biota (e.g. fungi vs. bacteria), mineralogy (aluminosilicates vs. opal and carbonate) and organic source materials (vascular plants vs. plankton). Refractory organic materials from both environments could be subjected to proxies for natural agents of oxic degradation such as fungal exoenzymes, high energy UV photo-oxidation (Skjemstad *et al.*, 1993) and $H_2O_2$.

### Fossil organic matter

The dynamics and radiocarbon contents of organic matter in both soils and sediments are difficult to model without including a significant fraction of refractory fossil carbon in TOC pools (e.g. Benoit *et al.*, 1979; Martens *et al.*, 1992; Trumbore, 1993). Molecular-level analyses of hydrocarbons in coastal marine sediments also indicate the presence of rearranged structures indicative of ancient rocks that have been heated during deep burial (Barrick and Hedges, 1981; Rowland and Maxwell, 1984). Recycling of kerogen-like material through soils and sediments might help explain the low percentages of TOC that can be accounted for by biochemical analysis (e.g. Figure 8). The amounts and types of fossil organic matter occurring in sediments and soils are important considerations not only for carbon turnover and radiocarbon-based studies, but also for interpretations of elemental and NMR data and appropriate normalization of biochemical concentrations. In addition, fossil organic matter must be discriminated from recently biosynthesized hydrolysis-resistant biomacromolecules and charcoal to assess mechanisms of organic matter preservation in both soils and sediments.

Even crude quantification of kerogen-like fossil organic matter in complex soil and sedimentary mixtures has been difficult. The highly condensed bulk material is challenging to measure at the molecular level and shows up only weakly as it dilutes $^{14}$C from other sources. Although detectable by CP/MAS $^{13}$C NMR, alkyl and aromatic carbon components of defunctionalized kerogens are difficult to discriminate from similar structures of modern origin such as charcoal. Chemical fractionations based on inertness toward extraction or hydrolysis provide one means of testing for fossil OC (Scharpenseel and Becker-Heidmann, 1992). A promising new approach is isolation of specific organic compounds via chromatographic separations, followed by $^{14}$C analysis by accelerator mass spectrometry (Eglinton *et al.*, 1996). This technique can be combined with pyrolysis (Goñi and Eglinton, 1994) to free structurally characteristic reaction products from fossil material prior to $^{14}$C determinations.

### Analytical approaches

Although few if any analytical techniques are used exclusively by only soil or sedimentary organic geochemists, both fields might benefit from a more balanced application of available methods. An example of a method that could be utilized more in soil organic studies is irm-GC/MS for determining the stable carbon isotope compositions of individual organic molecule types in complex mixtures (e.g. Lichtfouse *et al.*, 1994b, 1997). This technique has already been applied to hydrocarbons from soils (Lichtfouse *et al.*, 1994a). Irm-GC/MS analyses of more polar lipids, amino acids and carbohydrates

have been actively practiced in aquatic studies for years (Freeman et al., 1989; Engel et al., 1993). This extension of the biomarker method is particularly well suited to studies of biochemical dynamics in soils following conversions between C3 and C4 vegetation. Knowledge of where and how fast "new" carbon flows in soils could reveal residence times within pools of individual biopolymers (glucose/cellulose, hemicellulose/xylose, valine/protein) and microbial metabolites (muramic or diaminopimelic acid/bacteria, glucosamine/chitin). Such information also would allow tests under more realistic field conditions of the turnover times presently being used in soil carbon storage models (e.g. Sørensen, 1981).

Likewise, CP/MAS $^{13}$C NMR methods (and other NMR-based techniques) could be much more widely used for marine sediments. Direct applications to organic-rich opal oozes, and likely to calcareous counterparts, are already feasible with little or no pretreatment (Fig. 9B). Likewise, methods developed for removing interfering paramagnetic elements from soils prior to analysis (Skjemstad et al., 1994b; Schmidt et al., submitted—b) should be similarly useful for marine sediments. One advantage arising from $^{13}$C NMR analysis of marine sediments would be that carbon-normalized yields of biomonomers (e.g. aldoses) from conventional molecular-level analyses could be compared to apparent concentrations of precursor biopolymers (e.g. polysaccharide-like substances) indicated by NMR in the bulk sample. Low recoveries of products might indicate physical protection of parent biopolymers within non-hydrolyzable organic materials, as are now known to occur in marine plankton (Gelin et al., 1996). Alternatively, highly unusual or altered precursors may be involved. $^{13}$C NMR data also could better constrain the stoichiometry of mineralization reactions within marine sediments by indicating the types of organic matter that disappear with increasing depth and age. The potential also exists, by comparison of molecular-level and CP/MAS $^{13}$C NMR analyses, to identify the major structural features of the large fractions of organic matter missing from conventional biochemical analyses. CP/MAS $^{13}$C NMR also has the potential to nondestructively identify spatially distinct "domains" on the scale of tens of nanometers or more. This application is based on contrasting relaxation times of carbons associated with different proton types. This method was used by Preston and Newman (1992) to discriminate free methylene carbons from aromatic and carboxyl structures associated with iron in forest soil, and might be useful for detecting polysaccharides and proteins sheltered within non-hydrolyzable macromolecules.

NMR methods might be well complemented by broadly representative characterizations, such as chemolysis/mass spectrometry, diffuse-reflectance infrared Fourier-transform (DRIFT) spectroscopy and X-ray photoelectron spectroscopy (ESCA), which can be applied to small samples with minimal pretreatment (Oades, 1989; Schnitzer, 1991). Application of in-source methylation reagents such as tetramethylammonium hydroxide (TMAH) in pyrolysis-based methods greatly reduces the biases and artifacts associated with this sensitive method, allowing increased recoveries of polar products, such as carboxylic acids and lignin phenols, which more closely reflect structural features of the parent macromolecule (Saiz-Jimenez, 1994; Clifford et al., 1995). DRIFT analysis can be done on less than a gram of untreated soil in a few minutes and selectively reflects the functionality of organic matter at the immediate surface of particles (Nguyen et al., 1991; Skjemstad et al., 1993). ESCA is similar to DRIFT in being specific for organic substances on surfaces, but resembles $^{13}$C NMR in the rich detail of structural information provided (Barr, 1994). Such techniques allow systematic studies of the composition of soil and sedimentary organic matter, especially on mineral surfaces, without the complications potentially involved with humic fractionation schemes.

Both soil and sedimentary studies could benefit by more and different means of fractionating organic and inorganic matter prior to chemical analysis. Separation methods based on size, density, charge and/or other physicochemical properties should be considered as more environmentally realistic alternatives to classical humic fractionations. Hydrodynamic particle sorting techniques in particular offer gentle, flexible, and naturally consistent separations across a wide size range (Fig. 3). Split-flow thin (SPLITT) cells can be used with gravitational forcing to separate particles in the 1–80 μm range (Fuh et al., 1994) and has the capability for processing kg-size samples (Keil et al., 1994c; Bergamaschi et al., 1997). Centrifugal SPLITT requires more sophisticated equipment, but can be used to separate and characterize particles of 0.01–10 μm size range (Fuh et al., 1992). Field-flow fractionation (FFF) operates on differences in particle diffusivity, cross-section, charge, magnetic susceptibility and other physical characteristics which can be sensitively controlled within the separator (Giddings, 1993, 1995). In its various forms, FFF is applicable throughout the colloidal and into the particulate size range (1 nm–100 μm), but only with small (< 1 mg) samples (Chittleborough et al., 1992). These methods could be applied to either dispersed individual particles or intact aggregates and can be followed by a variety of analytical techniques including ICP–MS. Gravitational SPLITT and FFF could be particularly useful in studies of colloids, which play central roles in both marine and soil environments.

A final analytical aspect that greatly limits useful comparisons of organic matter compositions among and between soil and sediments is the woefully limited use of reference materials. Most types of organic compounds are analyzed by different procedures, among which there are many variants that can greatly affect the final measurement. Even bulk measurements of elemental, spectroscopic, and stable isotopic compositions are subject to errors, biases, and analytical "drift" over time. To be able to confidently compare analytical results over time among laboratories and methods, it is critical that well defined reference materials be routinely measured as a common benchmark. It is not necessary that the reference materials be "standards" for which absolute organic compositions have been certified, or that they be universally representative. Considering that hundreds of millions of dollars are spent each year world-wide on studies of organic matter in sediments and soils, it is appalling that stable, well defined reference materials are not already in wide use. This glaring, but readily resolved, oversight is one of the greatest impediments to effective study of organic matter in soils and sediments today.

## OVERVIEW

New discoveries are taking place across the full front of organic geochemistry. Hydrolysis-resistant aliphatic biomacromolecules are being recognized in a wide variety of living organisms. Intimate, and seemingly protective, associations of organic substances with inorganic particles are now evident over a range of scales from individual molecules sorbed on mineral surfaces to coarse plant debris jacketed within aggregates. Mass balances and site studies on land and in the ocean indicate that such challenging substrates as kerogens, pollen and coals are subject to oxic degradation so severe that preservation must result from highly unusual structures or environmental conditions. As such recalcitrant substrates are destroyed, nitrogen-rich aliphatic remains of microorganisms are produced and preserved in association with fine grained minerals.

These observations, and recent perspectives on bulk chemical composition provided by solid-state NMR and other spectroscopic methods, are resulting in new paradigms across the soil and sedimentary sciences. Recognition that living organisms make myriad hydrolysis-resistant biomacromolecles reduces the temptation to invoke complex "heteropolycondensation" mechanisms to explain how biochemicals might be broken down to small structural units that recombine abiotically to generate the predominance of chemically inscrutable organic matter in soils and sediments. Given a feedstock of resistant natural products, environmental degradation can now be envisioned as a "one-way street" down

which lignin and other such biomacromolecules are incrementally degraded, to produce smaller more oxidized products (Ertel and Hedges, 1984; Amon and Benner, 1994). "Humification" thus may progress from biomacromolecule, through humin and protokerogen, to humic acid, fulvic acid and other dissolved stages, on the way to carbon dioxide and water. Given that 499 out of 500 organic carbons follow this pathway completely (Fig. 1), it should not be too surprising to find degradation intermediates of recalcitrant biomacromolecules lingering in soils and sediments.

Within this scenario of relentless chemical and physical erosion, the interactions of organic remains with mineral in soils and sediments take on a new, less passive role. Continuous weathering of rocks and organic debris produces smaller alteration products whose interactions progress from gravitational, to electrostatic, to chemical control (Fig. 3). When the scale of organic-mineral interaction approaches the size of the degradative agent (bugs, bacteria and exoenzymes), physical protection becomes possible. This generality holds especially for crosslinked biomacromolecules whose breakdown requires a concert of cleavages. Thus, where a substrate "hides out" within a mineral matrix may be more critical for its survival and chemistry.

The time is ripe for increased interaction among chemists studying the parallels and contrasts of organic matter in soils and sediments. Many common challenges exist which can be better attacked by increased exchanges of knowledge and techniques. Every effort should be made to facilitate contact between terrestrial and aquatic organic geochemists by encouraging and supporting shared meetings, journals, reference materials and research centers. Such efforts are especially timely now that financial and environmental resources are being stretched by unprecedented increases in world population and consumption.

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