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Role of the soil matrix and minerals in protecting natural organic materials against biological attack

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Abstract

Natural organic materials in soils consist of a complex mixture of different biochemicals exhibiting numerous morphologies and stages of biological oxidation. A continuum of decomposability exists based on chemical structure; however, this continuum can be altered by interactions with minerals within matrices capable of stabilising potentially labile organic matter against biological oxidation. Protection is not considered to equate to a permanent and complete removal of organic C from decomposition, but rather to a reduced decomposition rate relative to similar unprotected materials. The stabilisation of organic materials in soils by the soil matrix is a function of the chemical nature of the soil mineral fraction and the presence of multivalent cations, the presence of mineral surfaces capable of adsorbing organic materials, and the architecture of the soil matrix. The degree and amount of protection offered by each mechanism depends on the chemical and physical properties of the mineral matrix and the morphology and chemical structure of the organic matter. Each mineral matrix will have a unique and finite capacity to stabilise organic matter. Quantifying the protective capacity of a soil requires a careful consideration of all mechanisms of protection and the implications of experimental procedures.

Keywords: Soil organic matter; Soil mineralogy; Soil texture; Biological oxidation

1. Introduction

Numerous definitions of what is and what is not soil organic matter exist (e.g. Oades, 1988; MacCarthy et al., 1990; Stevenson, 1994; Baldock and Nelson, 1999). The definitions as outlined by Baldock and Nelson (1999) and summarised in Table 1 will be used in this paper. Briefly, the organic fraction of soil encompasses all biologically derived organic material located within or on the surface of the soil including thermally altered organic material. As such, the soil organic fraction consists of a heterogeneous mixture of organic matter (OM) originating from plant, microbial and animal residues.

OM may range in size and complexity from simple monomers or organic acids to mixtures of complex biopolymers aggregated together in the form of cellular debris. In addition, the chemical structure of each component biomolecule, whether simple or complex, can vary along a continuum of decomposition. The continuum ranges from unaltered structures, identical to those found in precursor tissues, through to highly decomposed materials with structures bearing little resemblance to those from which they were derived. As a result, the OM of soil is often divided into different pools based on its physical properties (size, density and location within the soil matrix), chemistry, and/or rates of decomposition. The most common fractionation schemes use particle size and/or density to separate particulate organic matter (POM) from the more decomposed and amorphous humus associated with soil minerals (e.g. Baldock et al., 1992; Hassink et al., 1997). Recent work has also focused on the identification and quantification of "inert organic C" in soil (Skjemstad et al., 1999). The definition of the various component fractions of OM as they will be used in this paper are given in Table 1.

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The diverse physical and chemical characteristics of OM in soil enable it to influence soil biological, physical and chemical properties (Baldock and Nelson, 1999). OM contributes significantly to soil resilience and provides the chemical energy and nutrients essential to the activity of soil biological systems. OM also contributes directly to soil cation exchange and buffering capacity and both directly and indirectly to soil structural stability, water retention and soil thermal properties. Each pool of OM in soil will contribute differently to the various functions identified (Baldock and Skjemstad, 1999). For example, particulate organic matter provides a source of energy and nutrients to the decomposer community, but contributes little to soil cation exchange capacity. To ensure optimum plant productivity on mineral soils, it is not only essential that adequate levels of OM be maintained, but also that adequate levels of the correct types of OM are present.

The total amount of OM and the amounts of each type of OM found in soil are determined by the difference between inputs to and losses from the soil. Definitions of the processes of carbon loss and transformation as they will be used in this paper are presented in Table 2. When considering the total organic C fraction of soils, inputs are dominated by the deposition of plant residues, and losses arise from the mineralisation of organic C. However, inputs to and losses from a particular OM component can include additional transformations. Inputs to the POM fraction include deposition of plant residues as well as microbial residues originating from the assimilation of organic C during decomposition. OM enters the humus fraction as remnants of the decomposition of POM and as organic C assimilated by the decomposer community and released as metabolic products (e.g. extracellular mucilage or dead cells). Losses of organic carbon from specific OM fractions result from

Table 1
Definition of soil organic matter and its various components (modified from Baldock and Nelson, 1999)

Component	Definition
Soil organic matter (SOM)	Total of all biologically derived organic matter residing within the soil matrix and directly on the soil surface including thermally altered materials
Living components	Organic materials associated with the tissues and cells of living plants, soil microorganisms and soil fauna
Non living components	
Dissolved organic matter (DOM)	Water soluble organic materials that are < 0.45 μm
Particulate organic matter (POM)	Organic fragements with a recognisable cellular structure derived from any source but usually dominated by plant derived materials
Humus	A mixture of amorphous organic materials containing identifiable biomolecules (e.g. polysaccharides, proteins, lipids, etc.) and non-identifiable molecules (e.g. humic substances)
Inert organic matter (IOM)	Highly carbonised organic materials including charcoal, charred plant residues, graphite, and coal

Table 2
Definitions of the processes of carbon input, transformation and loss and properties of soil organic matter as used in this paper

Process and properties	Definition
Deposition	Addition of organic C to the soil organic fraction
Alteration	Conversion of organic C from one chemical structure into a different one resulting from either enzymatic attack or chemical reactions
Mineralisation	Conversion of organic C to carbon dioxide via respiration
Assimilation	Incorporation of organic C into tissues of the decomposer organisms
Decomposition	Loss of a particular component of organic C. Decomposition is equal to the sum of alteration, mineralisation, and assimilation
Biological stability	Ability of organic C to resist enzymatic attack with increasing resistance corresponding to increased stability

the activity of the decomposer community and can occur through all of the processes associated with decomposition (Table 2). As a result, losses of OM from the total organic fraction or a particular OM component are controlled by their ability to resist biological attack by the soil decomposer community. The term biological stability will be used to describe this resistance to enzymatic attack, with increasing biological stability corresponding to increasing resistance.

The biological stability of OM in soil is controlled by the chemical structure of the OM and the existence of various mechanisms of protection offered by the soil matrix and soil minerals. Chemical structure is important because of its direct influence on rates of decomposition of OM (see examples cited by Oades, 1988,1989) and its importance in defining the strength with which mineral and organic soil components interact. Although this paper will focus principally on the mechanisms of protection offered by the soil matrix and soil minerals, an understanding of the chemical (e.g. chemical structure) and physical (e.g. size) characteristics of the different components of OM in soil and the changes associated with decomposition is important. The objectives of this paper were:

1. to describe the chemical and physical characteristics of the different forms of OM in soil and how these characteristics change with decomposition,
2. to review the mechanisms involved in the biological stabilisation of OM in soil by the mineral matrix and soil minerals,
3. to examine the concept that soils have a maximum protective capacity, and
4. to discuss how mechanisms of biological stabilisation control the chemical structure of OM in soil.

2. Chemical characteristics of soil organic fractions and changes associated with oxidative decomposition

Fig. 1 presents a schematic representation of the oxidative decomposition of OM in mineral soils based on particle size and density fractionation data of Baldock et al. (1992), and data collected for fungal and bacterial cultures by Baldock et al. (1990b).

OM enters the soil as pieces of organic debris having a chemical structure and C/N ratio similar to that of the materials from which they were derived and a particle size >20 μm. Nuclear magnetic resonance (NMR) spectroscopy can be used to differentiate the organic carbon on the basis of its chemistry (Table 3). Application of solid-state ^{13}C NMR to POM (soil particles >20 μm with a density <2.0 mg m^{-3}) shows that it is dominated by *O*-alkyl structures and has a chemistry consistent with the high contents of polysaccharides typically found in fresh plant and microbial tissues (e.g. cellulose, hemicellulose, chitin, peptidoglycan, etc.). As these organic particles are decomposed, the more labile components of the residues are preferentially utilised and particle size decreases leading to a concentration of the more chemically recalcitrant structures (e.g. lignin and alkyl structures) in the 2–20 μm size fraction. Since a significant proportion of the carbon assimilated by fungi and bacteria during decomposition ends up in *O*-alkyl microbial structures (Fig. 1), a complete disappearance of O-alkyl carbon is unlikely. However, the origin of the *O*-alkyl C should shift towards a greater dominance of microbially derived materials in progressing from the >20 μm fraction to the 2–20 μm fraction. Baldock et al. (1992) demonstrated that the increase in aromatic and alkyl C contents during this initial stage of decomposition could be explained by a selective utilisation of the plant derived *O*-alkyl C.

As the content of *O*-alkyl C decreases, the second stage of decomposition is initiated. Lignin is decomposed resulting in changes to the chemical structure of the residual lignin polymer and a reduction in the quantity of aromatic C (Baldock et al., 1997). The decomposition of lignin is performed dominantly by fungi but some bacteria can modify the nature of functional groups attached to lignin. Lignin degrading organisms do not gain energy or assimilate from lignin degradation (Haider, 1994), but benefit through an exposure of labile *O*-alkyl C buried within lignin/polysaccharide structures. The most biologically stable form of organic carbon found in soils is alkyl-C (Paul and Van Veen, 1978). However, provided the appropriate organisms are present, even this material could be decomposed and mineralised.

The extent to which OM progresses through the stages of decomposition depicted in Fig. 1 will depend on the presence of protection mechanisms capable of enhancing biological stability. Where no protection mechanisms are operative, such as in well-aerated peat or forest litter layers, biological stability will be entirely controlled by the recalcitrance offered by the chemical structure of the OM. Under such conditions, essentially all organic C associated with a given input of OM will be mineralised, provided the appropriate suite of organisms exists to degrade all forms of organic C present. However, in soil containing minerals, the entire organic fraction or specific organic components may accumulate in response to the presence and nature of mechanisms of protection offered by the soil matrix and minerals.

3. Mechanisms of biological protection by the soil matrix and mineral particles

The mechanisms of biological protection of OM in soil containing mineral particles operate at size scales ranging from micrometres to centimetres and are dependent on the chemical properties of the mineral constituents and the three dimensional arrangement of

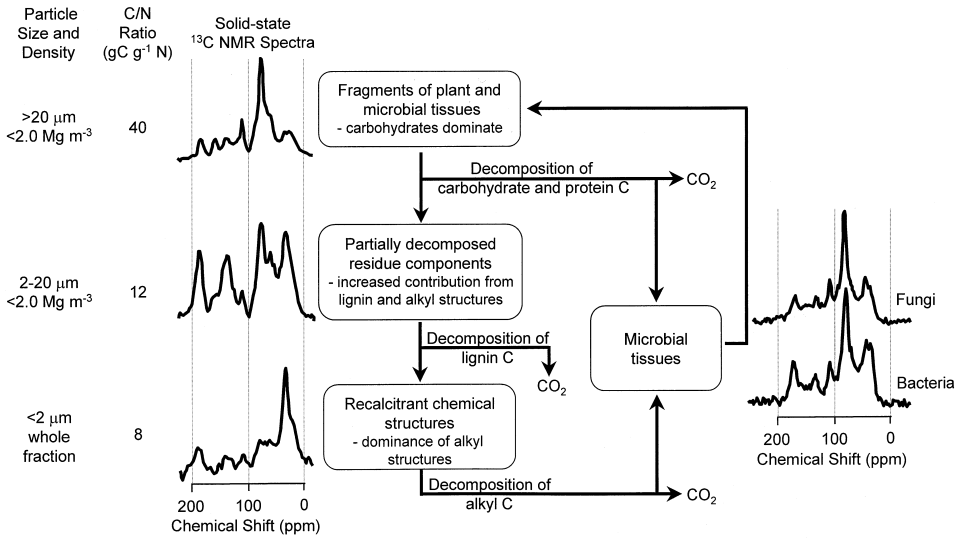

Fig. 1. Changes in particle size, C/N ratio and chemical composition of organic matter in mineral soil with increasing extent of oxidative decomposition (modified from Baldock et al., 1992 using data from Baldock et al., 1990). The data presented for the >20 μm and 2–20 μm fractions were obtained from the <2.0 Mg m^{-3} components of those fractions. Data presented for the <2 μm fraction were obtained from the whole fraction.

mineral particles. The various mechanisms of protection can be attributed to the following three general characteristics of the soil mineral matrix:

1. the chemical nature of the soil mineral fraction and the presence of multivalent cations,
2. the physical nature of the soil mineral fraction, especially the presence of surfaces capable of adsorbing organic materials, and
3. the architecture of the soil matrix.

Each of these mineral matrix characteristics will be addressed in the subsequent sections of this paper.

3.1. Chemical nature of the soil mineral fraction and the presence of multivalent cations

A comparison of the organic C contents of different types of mineral soils indicates that the presence of $CaCO_3$ or amorphous Al and Fe leads to accumulations of organic C in comparison to other soil types (Spain et al., 1983; Oades, 1988; Sombroek et al., 1993). Using data derived from Spain et al. (1983), Oades (1988) demonstrated a positive relationship between soil organic C contents and either high base status or the presence of substantial contents of Al and Fe oxides. Many additional soil characteristics capable of affecting organic C contents (e.g. clay content) can also increase with increasing base status; however, Oades (1988) also noted that calcareous sands had higher organic C contents than siliceous sands (15–40 mg C g^{-1} versus <5–15 mg C g^{-1}, respectively).

Duchaufour (1976) suggested that the presence of reactive $CaCO_3$ in soils can lead to a biological stabilisation of both POM and humus. The formation of thin carbonate coatings visible under magnification was suggested for fresh residues, and a precipitation induced by the formation of Ca-organic linkages was suggested for the more decomposed humus. Stabilisation of OM in high base status soils with less reactive $CaCO_3$ must result primarily from the formation of Ca-organic linkages. The ability of a source of Ca^{2+} cations to protect soil organic matter from mineralisation has been well demonstrated. Sokoloff (1938) showed that addition of salts containing Ca reduced the solubility and mineralisation of organic C relative to the addition of either no salt or Na^{+} salts (Fig. 2). Muneer and Oades (1989c)

Table 3
Types of organic carbon found in various chemical shift regions of a solid-state ^{13}C NMR spectrum

Chemical shift range (ppm)	Types of carbon
0–45	Alkyl C
45-65	*N*-alkyl and methoxyl C
65–95	*O*-alkyl C
95–110	Di-*O*-alkyl C
110–145	Aromatic and unsaturated C
145–160	Phenolic C
160–190	Amide and carboxyl C
190–220	Aldehyde and ketone C

also observed a decreased solubility of soil organic C on addition of Ca^{2+} salts, and additional studies (Linhares, 1977; Muneer and Oades, 1989a,b) have noted a decreased mineralisation of C from an added substrate or native organic matter on addition of salts containing Ca to soils (Fig. 3).

In studies where the mineralisation of soil organic C was measured after addition of Ca containing salts, the question remained as to whether the protection was derived from the formation of Ca-organic linkages or from indirect effects of Ca^{2+} on colloidal dispersibility. Direct evidence for an enhanced biological stability of organic C through the formation of Ca-organic linkages was demonstrated by the following results: (1) reduced oxygen absorption during the incubation of Ca^{2+} saturated humates relative to Na^{+} saturated humates (Juste and Delas, 1970, Juste et al., 1975), (2) a three fold increase in the mineralisation of C from an organic soil after replacing Ca^{2+} cations with K^{+} (Gaiffe et al., 1984), and (3) an increased mineralisation of plant residues with increasing sodicity (Nelson et al., 1996). Since addition of Ca^{2+} cations to soil did not alter the rate of glucose decomposition (Baldock and Oades, 1989), it is probable that Ca^{2+} forms linkages with the products of microbial decomposition processes rather than the undecomposed precursors.

Soils derived from volcanic ash (Andisols) contain high contents of allophane and are characterised by large accumulations of organic C. The formation of Al-organic complexes has been postulated to provide a mechanism for stabilising OM against biological attack. The source of the Al may be Al^{3+}, Al-hydroxy cations or terminal Al atoms available for bonding within allophanic minerals. The ability of Al^{3+}/Al-hydroxy cations to form biologically stable Al-organic complexes was demonstrated in incubation experiments where oxygen consumption and C mineralisation rates from a variety of Al and Fe saturated organic compounds were measured (Martin et al., 1966, 1972; Juste et al., 1975).

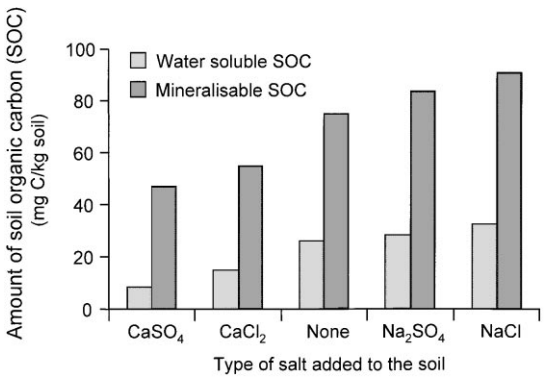

Fig. 2. Influence of adding calcium and sodium salts on the amounts of water soluble and mineralisable soil organic carbon during a 45 day incubation (Sokoloff, 1938).

The role of allophanic minerals in protecting OM against biological attack was demonstrated in studies where C mineralisation was measured from allophanic soil, nonallophanic soil, and nonallophanic soil amended with allophane (Zunino et al., 1982; Boudot et al., 1988,1989). In each of these studies, mineralisation of C derived from added substrates was reduced by the presence of allophane. Zunino et al. (1982) also demonstrated that the chemical structure of the substrate contributed to the degree of biological stabilisation imparted by the presence of allophane (Fig. 4). A protective influence of allophane on soil OM was shown by Boudot et al. (1986,1988). A significant correlation was obtained between the amount of organic C mineralised and the contents of amorphous Al and allophane, but not with clay or exchangeable Al^{3+}. The presence of amorphous Fe minerals and Fe^{3+} cations can also offer

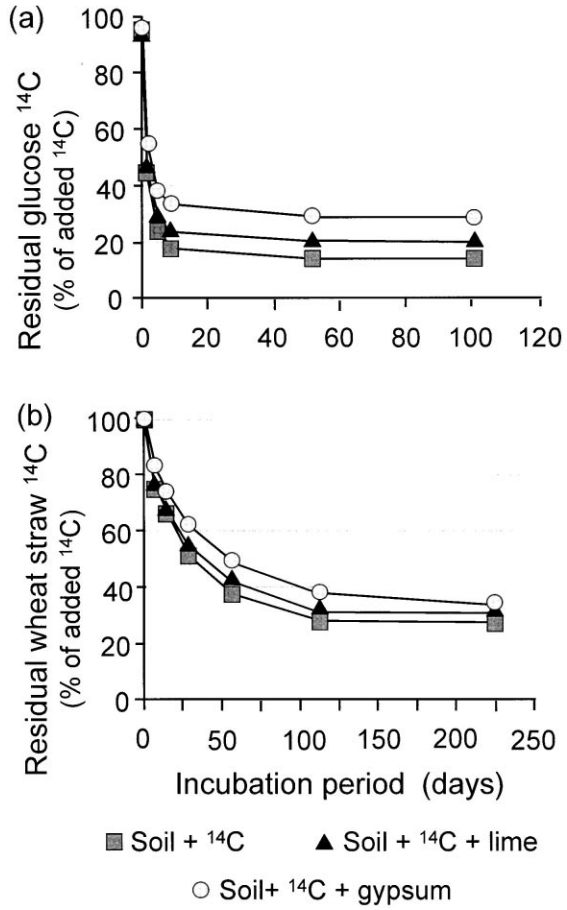

Fig. 3. Residual substrate ^{14}C remaining after incubating unamended soil and soil amended with agricultural lime ($CaCO_3$) or gypsum ($CaSO_4 \cdot 2H_2O$) in (a) a laboratory incubation with ^{14}C-glucose (modified from Muneer and Oades, 1989a,b) a field incubation with ^{14}C-wheat straw (modified from Muneer and Oades, 1989b).

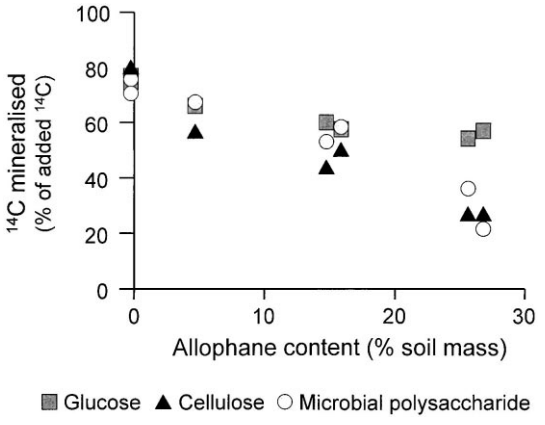

Fig. 4. Influence of allophane content on the amount of ^{14}C-labelled glucose, cellulose and microbial polysaccharide carbon that was mineralised in a laboratory incubation (Zunino et al., 1982).

protection against biological attack, but the effects are not as great as those noted with the corresponding forms of Al (Juste et al., 1975; Boudot et al., 1989).

The presence of mutivalent cations can also indirectly impact on the biological stability of OM in soils. Clay particles saturated with multivalent cations tend to remain in a flocculated state reducing the exposure of OM adsorbed on clay particle surfaces or existing as globules between packets of clays within a clay matrix to biological attack. In addition, the three-dimensional orientation of organic macromolecules containing carboxyl functional groups may be altered in the presence of multivalent cations. The structures will become more condensed and the orientation of functional groups will be altered (Oades, 1988). Such changes may alter the efficiency of enzymatic attack.

3.2. Presence of mineral surfaces capable of adsorbing organic materials

The specific surface area (SSA) of soil mineral particles increases in progressing from large to small particles. Ransom et al. (1998) demonstrated the significant effect that even small amounts of high SSA (100 $m^2\ g^{-1}$) clay-size (<2 μm) material can have on the total SSA of mineral particle mixtures. The presence of 1 wt.% of high-SSA clay in 1 mm diameter sand grains with a SSA of 0.001 $m^2\ g^{-1}$, increases total SSA by three orders of magnitude. The relative magnitude of the effect of adding high-SSA clays to non-clay mineral particles decreases as the size of the non-clay mineral particles decreases. Approximately 5 wt.% of high-SSA clay is required to increase the SSA of 2–4 μm silt particles by 50%. Using calculations such as these, it becomes apparent that the presence of clay particles in soil provides the most significant surface area onto which OM may be adsorbed.

The mineralogy, surface charge characteristics, and precipitation of amorphous Fe and Al oxides on clay mineral surfaces give clay minerals a capacity to adsorb OM. Such adsorption reactions provide a mechanism of stabilising organic matter against biological attack. Many positive correlations have been obtained between the content of native soil organic C and clay content (e.g. Schimel et al., 1985a,b; Spain, 1990; Feller et al., 1991) and between the amount of residual substrate C retained in a soil and clay content (e.g. Amato and Ladd, 1992). The various potential interactions between inorganic particles and OM in mineral soils have been summarised by Oades (1989).

Ladd et al. (1985) monitored the mineralisation of carbon from ^{14}C labelled plant materials added to four cultivated soils having similar mineralogies but different clay contents (5–42%). The labelled residues were left to decompose in the field for 8 years in the absence of any other organic additions. The amounts of residual labelled plant carbon and residual native soil organic C remaining after the incubation were proportional to soil clay content (Fig. 5). In a similar experiment, Saggar et al. (1996) monitored the amount of residual ^{14}C-labelled ryegrass carbon in four soils of variable mineralogy over a 6 year period. The mean residence time of the added ^{14}C labelled ryegrass C was not a function of clay content, but was strongly correlated with the specific surface area (SSA) as determined using *p*-nitrophenol (Fig. 6). Since the mineralogies of all of the soils used by Ladd et al. (1985) were similar, it would be likely that clay content and SSA were well correlated. Sørensen (1975) also demonstrated the importance of SSA in defining the biological stability of OM in soil. Addition of high SSA montmorillonite to a soil/sand mix stabilised microbial metabolites to a greater extent than addition of low SSA kaolinite. Skene et al. (1996) showed that over a period of 170 days, a decrease in the decomposition of straw occurred with the inclusion of a mineral matrix such as sand, kaolinite or a loamy sand. The relative amounts of microbial biomass also increased, suggesting that these matrices also provided protection for micro-organisms.

Recent studies on the preservation of organic carbon in marine sediments also identify SSA and mineralogy as important variables (Keil et al., 1994; Mayer, 1994a,b). Using data from Keil et al. (1994) for the Washington State continental margin, Ransom et al. (1998) demonstrated that total organic C (TOC) in the sediments was linearly related to SSA as well as the content of high surface area minerals present (smectite + illite + opal) (Fig. 7a). Changes in the mineralogy of the high SSA minerals present in the samples used by Keil et al. (1994) were minor. Ransom et al. (1998) examined the relationship between total organic carbon and SSA for marine sediments in which the SSA was dominated by mineral particles with different mineralogies, in particular variations in the content of smectite.

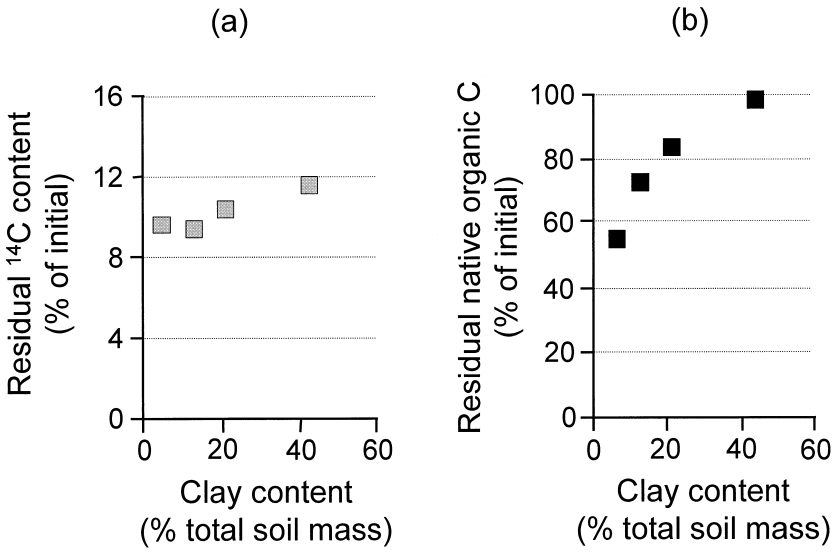

Fig. 5. Influence of clay content on the recovery of (a) residual ^{14}C-labelled carbon and (b) residual native carbon remaining eight years after addition of ^{14}C labelled plant materials to soils having a similar mineralogy (Ladd et al., 1985).

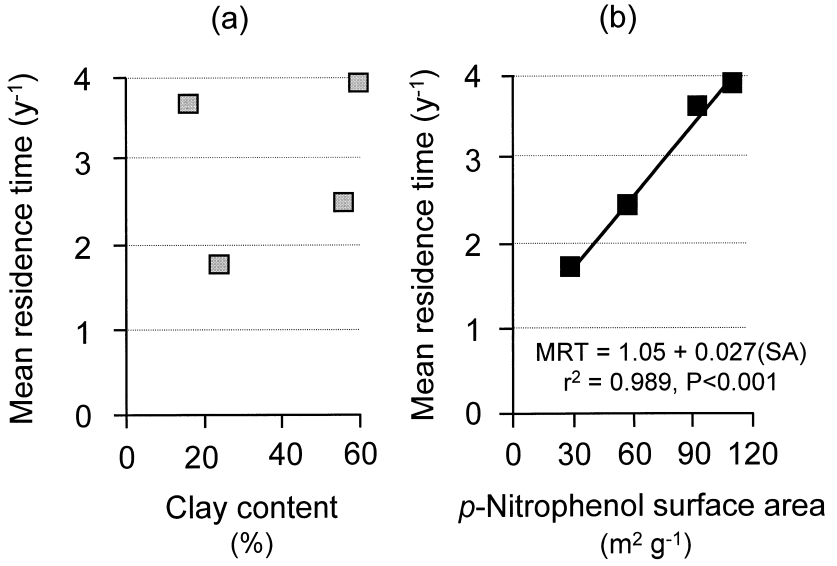

Fig. 6. Relationship between mean residence time of ^{14}C-labelled ryegrass incubated for 6 years in soils with a variable mineralogy and (a) soil clay content and (b) soil surface area as determined by *p*-nitrophenol (Saggar et al., 1996).

The relationship between TOC and SSA differed with variations in mineralogy. The low smectite sediments showed little variation in TOC with increasing SSA, and the high smectite sediments showed much larger variations in TOC across a narrow range of SSA (Fig. 7b). Different behaviours were also obtained when the TOC of the clay fraction was plotted against SSA of the clay fraction (Fig. 7c). The linear but significantly different relationships obtained between clay-TOC and clay-SSA for each type of sediment mineralogy indicated that a relationship existed between SSA and protection of organic C, but that mineralogy exerted a strong control over the relationship.

Mayer (1994a,b) and Keil et al. (1994) proposed that the organic C associated with mineral grains in marine sediments existed as a monolayer spread evenly over the entire surface. Using transmission electron microscopy Ransom et al. (1997) showed that the organic matter

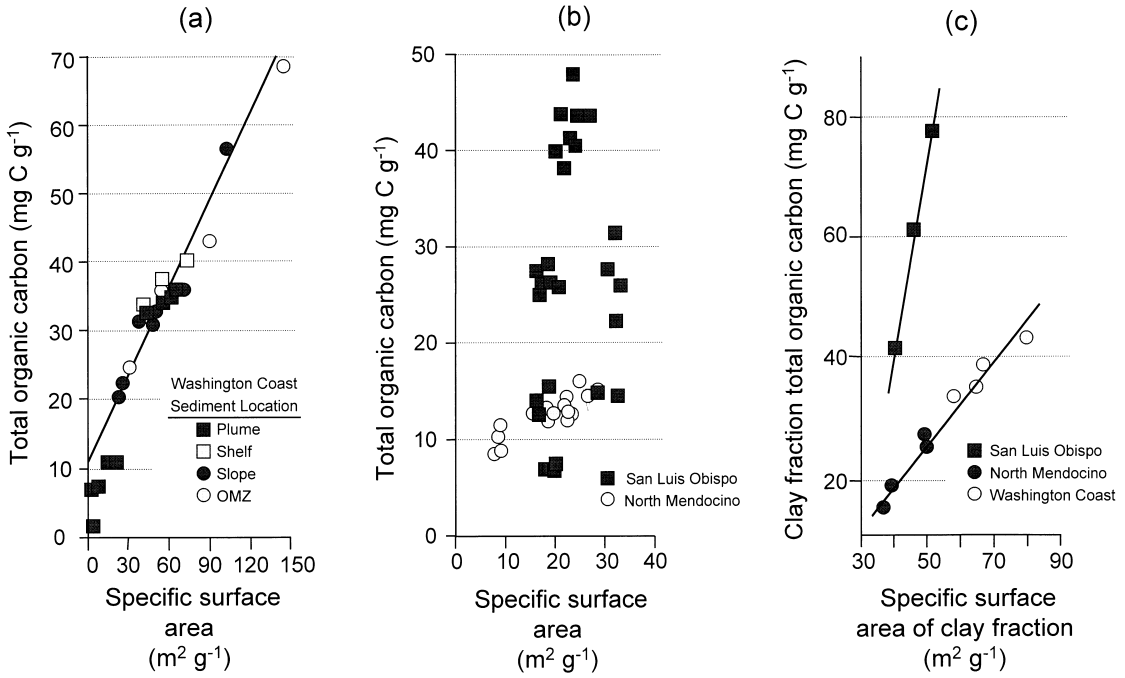

Fig. 7. (a) Correlation between surface area and total organic carbon content of marine sediments collected from the Washington continental margin (data from Keil et al., 1994, figure modified from Ransom et al., 1998). (b) Correlation between surface area and total organic carbon of marine sediments collected from transects off the California continental margin (modified from Ransom et al., 1998). The San Luis Obispo samples had >21% smectite (average ~26%) and the North Mendocino samples had <13% smectite (average ~8%). (c) Relationship between total organic C content of the clay fraction and surface area of the clay fraction for the California and Washington continental margin sediments (modified from Ransom et al., 1998).

existed in patches associated with and often encapsulated by mineral surfaces and was not uniformly spread over all surfaces. Subsequent work (Mayer, 1999) has shown that at low to moderate organic carbon loadings (3 mg organic C m^{-2}), marine aluminosilicate sediments had <22% of their surfaces coated with organic materials.

A dependence of protection of organic C in mineral soils on the mineralogy of the <20 μm fraction was demonstrated by Feller and Beare (1997). Different relationships between total soil organic C content and the wt.% of the <20 μm mineral fraction were obtained for tropical soils containing low activity clay (kaolinitic/halloysitic), high activity clay (smectitic) and allophanic minerals.

The mineralogy of soil particles, in particular that of the clay fraction, exerts its control over protection of OM through its effect on the type and density of active sites capable of adsorbing organic materials and the extent to which the clays are maintained in a stable flocculated state. The presence of oxy-hydroxides of Al and Fe and increases in surface charge density, originating from either isomorphic substitution or pH-dependent charges, will increase the reactivity of the mineral surface and the potential adsorptive and protective capacities. Flocculation of clay particles, particularly into open structures formed through edge/face interactions, can effectively trap and isolate OM from decomposer organisms. There is some evidence that organic matter can become trapped within the interlayer spaces between individual sheets of layer silicate clay minerals (Theng et al., 1986); however, no additional occurrences of such a phenomenon have been documented. It is, therefore, unlikely that such OM would constitute a significant portion of the organic fraction of most mineral soils.

3.3. Architecture of the soil matrix

The architecture of the soil mineral matrix refers to the arrangement of pores and soil particles. Soil architecture can influence the biological stability of organic materials through its effects on water and oxygen availability, entrapment and isolation of organic materials from decomposer organisms, and the dynamics of soil aggregation.

All OM in soil is located within the pore space as discrete particles or molecules adsorbed onto soil particles. Since decomposition and mineralisation processes occur within the pore space, the proportion of the soil volume occupied by pores and the distribution of pore

sizes can influence the biological stability of organic materials in soil.

The pore space of soil is composed of a continuum of pores ranging in size from micropores <0.1 μm in diameter through to macropores >20 μm with an upper size limit on the order of centimetres. Adequate quantities of available water and oxygen are required to optimise the processes of decomposition and mineralisation. Since the total amount of pore space and the pore size distribution of the soil matrix control the availability of water and oxygen, these soil architectural properties exert a control over decomposition and mineralisation. With increasing water content, water becomes more available to decomposer organisms; however, oxygen availability decreases. An optimum air-filled porosity exists at which the processes of decomposition and mineralisation of organic C will be optimised for a given soil (Fig. 8). Changes in the pore size distribution towards a greater proportion of large pores, such as noted in progressing from a clay to sand, are accompanied by higher rates of C mineralisation at equivalent values of air filled porosity (Franzluebbers, 1999) (Fig. 8). Franzluebbers (1999) also showed that reducing total porosity by compression induced reductions in C mineralisation at all levels of air-filled porosity and shifted the air-filled porosity at which C mineralisation was maximised (Fig. 8). Similar effects of pore size distribution, air-filled porosity and volumetric water content on mineralisation of C and N have been observed by Stanford and Epstein (1974), Lin and Doran (1984), and Thomsen et al. (1999).

The pore size distribution of a soil also influences the ability of decomposer organisms to reach potential organic substrates. Kilbertus (1980) suggested that bacteria can only enter pores >3 μm. Irrespective of the actual size limit imposed, a lower limit of pore size into which organisms cannot enter undoubtedly exists. Within pore sizes less than this lower limit, decomposition of OM can only occur via diffusion of extracellular enzymes away from organisms towards a substrate and then diffusion of the products of enzyme reactions back to the organisms. With increasing clay content, the proportion of the total porosity found in small pores increases, and the potential stabilisation of OM against biological attack due to the exclusion of decomposer organisms increases. The concept of exclusion, based on the physical size of the decomposer organisms, can be extended to predation of micro-organisms by soil fauna. van der Linden et al. (1989) showed that protozoa and nematodes are excluded from pores <5 μm and <30 μm, respectively. Thus OM residing in pores smaller than these diameters in the form of molecules, small particles, or bacterial or fungal tissues will not be susceptible to decomposition or predation by soil fauna. Killham et al. (1993) demonstrated that when glucose was placed in pores <6 μm, the turnover of glucose C incorporated into the microbial biomass was slower than when the glucose was placed in pores <30 μm.

Scanning electron micrographs of clay-organic matrices in soil indicate that OM is not uniformly distributed in soil matrices and that much of the OM is not in direct contact with or intimately associated with mineral surfaces. OM can exist as discrete particles, masses of amorphous materials typified by the mucilage exuded by microorganisms, or individual molecules adsorbed to mineral particles (Ladd et al., 1993; Ransom et al., 1997). Thus, encapsulation of OM by flocculation of clay particles, adsorption of mineral particles around organic particles, or formation of stable aggregates will influence the biological stability of OM. Encapsulation can occur at size scales ranging from nanometres (e.g. encapsulation of OM into pores between packets of clay particles) to centimetres (e.g. encapsulation of a piece of plant residue by mineral particles). Encapsulation operates at small size scales by placing a physical barrier between potential substrates and decomposer organisms or their

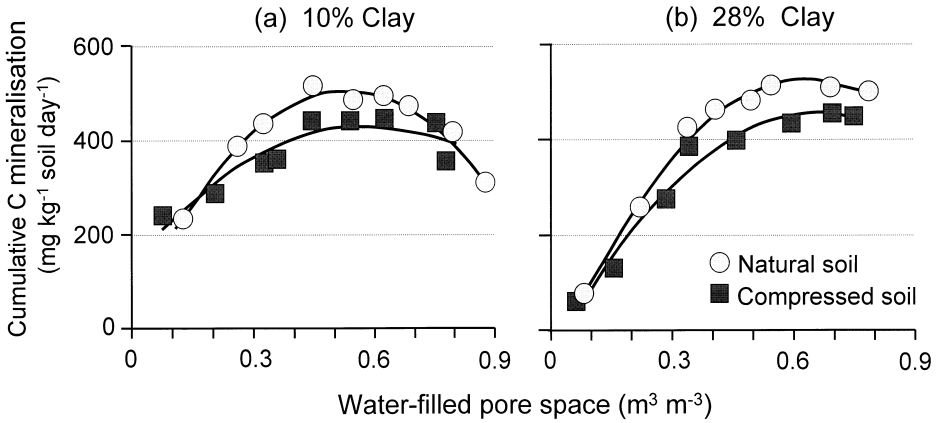

Fig. 8. Changes in mineralisation of C with changes in air-filled porosity and for uncompressed and compressed soils with (a) 10% clay and (b) 28% clay (modified from Franzluebbers, 1999).

extracellular enzymes. At large size scales (e.g. a piece of root encapsulated by clay), decomposer organisms will be associated with the surface of the organic particles and encapsulation may restrict decomposition by limiting the movement of oxygen to sites of active microbial activity.

Soil mineral particles are typically bound together into larger secondary particles referred to as aggregates, except in sandy soils where aggregates may not exist. Relative to the larger pores between aggregates, the smaller internal pores are likely to remain filled with water and restrict oxygen availability. Sexstone et al. (1985) showed that the interior of aggregates could be anaerobic under well-aerated conditions. The presence of organic cores within aggregates (Beare et al., 1994a, b; Golchin et al., 1994, 1998) will enhance these effects by increasing the biological oxygen demand within the aggregate interior. Soil aggregation is a transient property and aggregates are continually being formed and destroyed. The protection of OM against biological attack by encapsulation within an aggregate will be greatest where aggregate stability is high and aggregate turnover is low. Amelung and Zech (1996) demonstrated the influence of aggregation on the biological stability of OM. OM buried within aggregates had a higher C/N ratio, higher content of less biologically altered lignin, and a higher content of neutral sugars than OM associated with the 0–0.5 mm external layer of aggregate surfaces (Table 4).

4. Capacity of mineral soils to protect organic matter

The three mechanisms involved in the protection of OM against biological attack in soil are determined by the mineralogy and size distribution of soil mineral particles. For each mechanism, only a finite amount of OM can be protected. As a result, each soil will have a finite capacity to protect OM against biological attack. The proportion of OM added to a soil that can be protected will depend on the extent of saturation of the protective capacity. In soils where the protective capacity is not saturated, further additions of OM will increase soil OM contents. Where the protective capacity is saturated, OM added to the soil will remain in a biologically available form, be mineralised provided the appropriate suite of decomposer organisms and environmental conditions are present, and contribute little to soil OM content.

It is important to recognise that protection rarely equates to a permanent and complete removal of organic C from the decomposing pool, but rather equates to a reduction in the rate of decomposition relative to the same form of C existing in an unprotected state. One exception to this generalisation may be the potential trapping of OM within the interlayer spaces of layer silicate clay minerals (Theng et al., 1986). As protected OM is slowly mineralised, its position in the protected pool is filled with new OM provided a source of the correct type of OM exists.

Studies that have attempted to quantify the protective capacity of soil have only focused on the ability of mineral surfaces to adsorb OM (e.g. Hassink, 1997; Hassink et al., 1997). Less consideration has been given to quantifying the roles of soil chemical properties or the architecture of the mineral matrix. Hassink (1997) postulated that the protective capacity of a soil could be estimated by measuring the amount of organic C and N associated with the <20 μm (clay + silt) particle size fraction of sandy soils under long term pasture production. Although the organic C content of the <20 μm particle size fraction differed between the two sandy soils, it was not influenced by either cultivation or soil depth within each soil type (Fig. 9). Hassink (1997) interpreted these results to indicate that the amount of organic C that can become associated with the <20 μm particle size fraction had reached a maximum in all soils.

The procedure used by Hassink (1997) to prepare the soils for size fractionation included a 24 h soaking in water followed by a 15 min ultrasonic treatment. Under such preparative conditions, dispersion of soil mineral particles would be virtually complete, especially for sandy soils, and the potential for a redistribution of organic C within the soil particles would be high. Golchin et al. (1994) observed that approximately 50% of the light fraction organic carbon had broken up and was

Table 4
Organic carbon contents and chemical properties of organic matter isolated from the exterior 0.5 mm layer of soil aggregates and from aggregate interiors collected along a north-south transect through the North America prairies (Amelung and Zech, 1996)

	Organic C content (g C kg^{-1} fraction)	C/N[a] ratio	Lignin[b] VSC (g kg^{-1} SOC)	Lignin[c] $(Ac/Ad)_v$	Neutral sugars (g C kg^{-1} fraction)	$\frac{G+M^d}{X+A}$
Aggregate interior	22.3	10.1	16.2	0.22	4.38	0.76
Aggregate exterior	20.3	9.5	12.1	0.31	3.90	0.87

[a] Mass ratio of organic C to total N.
[b] Determined by CuO oxidation.
[c] Mass ratio of acid to aldehyde forms of the vanillyl for of the lignin monomers released by CuO oxidation.
[d] Mass ratio of (galactose + mannose) to (xylose + arabinose) monomer contents.

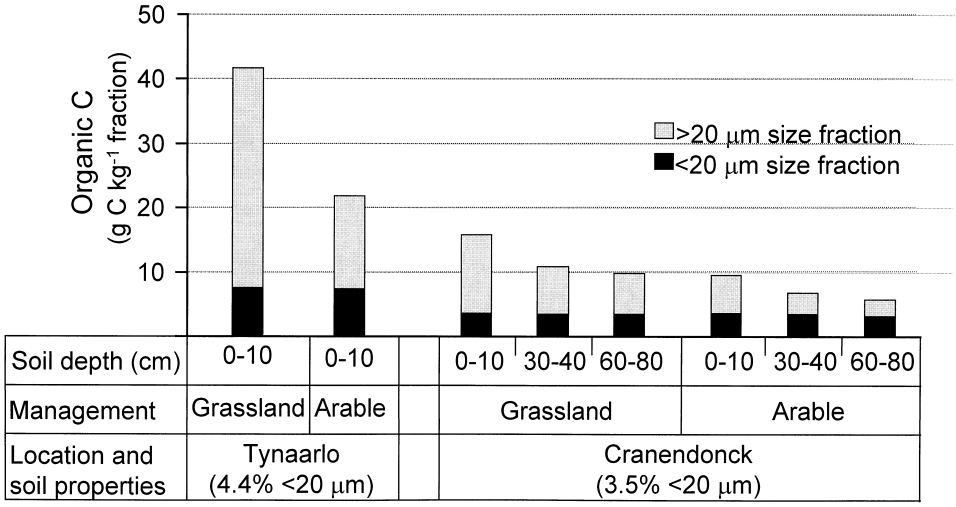

Fig 9. Content of organic C associated with the >20 μm and <20 μm particle size fractions of two sandy soils under grassland and arable management (data from Hassink, 1997).

redistributed after a 10 min ultrasonic treatment. The question also arises as to the fate of globules of OM previously encapsulated within the mineral matrix prior to ultrasonic dispersion, and the impact of exposing potentially reactive mineral surfaces to a suspension in which small particles and molecules of OM may be in solution. It is possible that the constant content of organic C in the <20 μm fraction was a function of the dispersion methodology and not due to a saturation of the potential sites of OM adsorption. Whether this is indeed the case or not, the fact still remains that the dispersion treatment utilised by Hassink (1997) only allowed the capacity of the <20 μm fraction to adsorb OM to be quantified, and excluded the potential OM that may be associated with the <20 μm fraction due to encapsulation. In studies that attempt to define the protective capacity of soil towards OM, careful consideration must be given to the mechanisms of protection associated with soil chemical and architectural properties.

5. Implications of protection on the chemical character of soil OM.

Under conditions where the soil matrix or soil minerals offer no biological protection to OM, the extent and rate of oxidative decomposition would be determined by the chemical recalcitrance of the OM and would follow a pattern similar to that depicted in Fig. 1. The chemical structure of OM under such conditions will be a reflection of the ability of decomposer organisms to degrade and mineralise the OM added to the soil.

The presence of mineral particles capable of protecting OM will perturb the progression from less to more chemically recalcitrant materials during decomposition. OM with potentially labile chemical structures can be removed from the biologically available pool of OM by the mechanisms of protection offered by the soil matrix or soil mineral particles. The chemical structure of the soil OM will then take on a different character from that which would have existed in the absence of protection mechanisms. Instead of being governed solely by the chemical recalcitrance of the organic residues added to the soil, the chemical structure will include a greater proportion of OM derived from the potentially labile chemical structures stabilised by interactions with soil

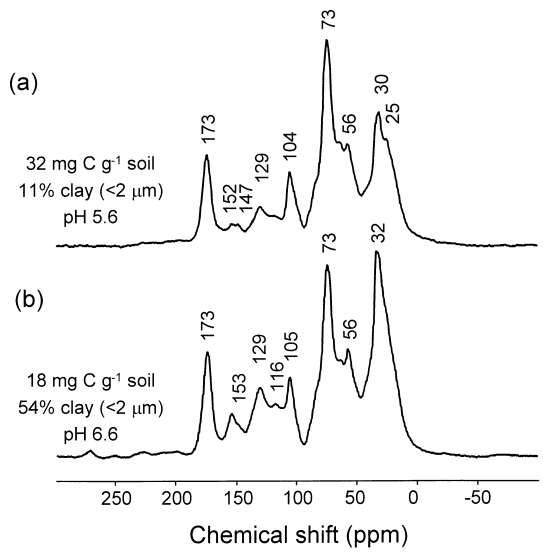

Fig. 10. Solid-state ^{13}C NMR spectra acquired for two Australian soils with (a) 11% clay and (b) 54% clay.

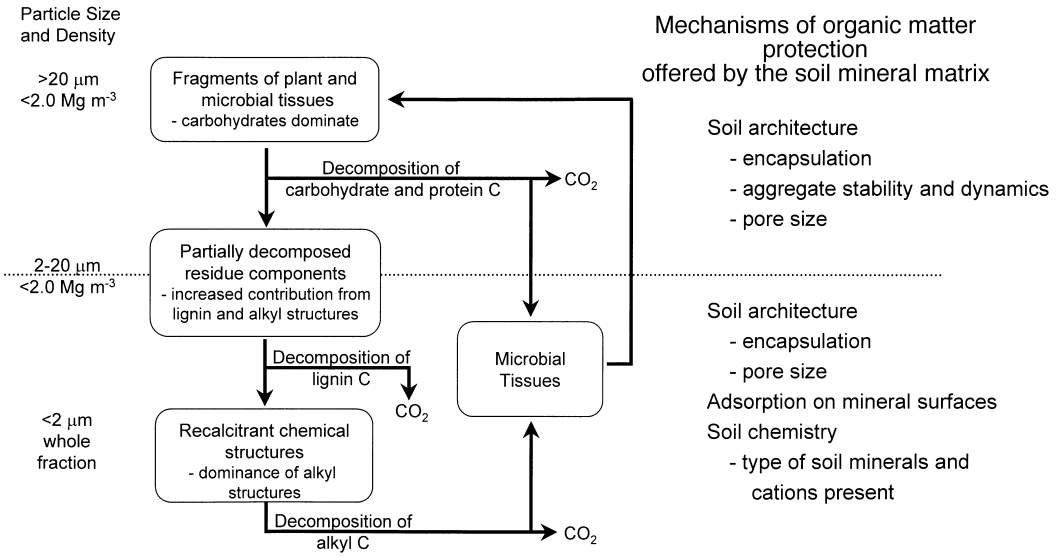

Fig. 11. Summary the role of the soil mineral matrix in protecting natural organic materials against biological attack and the major types of organic matter that can be protected by each mechanism. Refer to Fig. 1 for the parallel changes in chemical composition of natural organic materials.

minerals or protected by their position in the soil matrix.

To demonstrate the impact of protection on the chemical character of soil OM, the chemical character of the OM associated with two soils having different clay contents will be examined. The solid-state ^{13}C NMR spectra collected from a soil with 11% clay and a soil with 54% clay are presented in Fig. 10. In the low-clay soil, less capacity would exist to protect OM by adsorption onto mineral surfaces and encapsulation within the mineral matrix at a scale <20 μm, and a greater proportion of the products of biological oxidation of particulate organic materials will be mineralised. An accumulation of organic carbon content to 32 g C kg^{-1} soil, under conditions of low protection via adsorption and encapsulation, could only result from an increased contribution of particulate debris to the soil organic fraction, either through increased inputs or the input of residues with a chemically recalcitrant structure. In the high-clay soil, protection of the products of biological oxidation via adsorption reactions and encapsulation at a small size scale (<20 μm) would be greater than that in the low clay content soil. Thus, at an organic carbon content of 18 g C kg^{-1} soil, a greater proportion of the soil organic fraction should be matrix-protected amorphous organic materials that have been processed biologically. A greater plant-like chemical structure of the organic carbon in the low clay soil, and the more highly processed nature of carbon in the high clay soil are consistent with the acquired ^{13}C NMR spectra. Although the observed chemical structure of organic carbon in the two soils is consistent with the extent of protection offered by the soil clay fraction, additional factors (e.g. amount and quality of the organic materials added to the soil, species composition of the decomposer community, temperature, availability of water and nutrients, etc.) may also be important.

6. Conclusions

Mineral particles and the architecture of the soil matrix exert control over soil OM content through mechanisms that protect either organic inputs or their decomposition products against biological attack. The capacity of each mechanism to protect OM is finite and a function of soil chemical properties, the size and mineralogy of mineral particles, and the three dimensional arrangement of mineral particles and pore space in the soil volume. To define the protective capacity of soils towards OM, it is essential to consider the implications that experimental methodologies will have on all protection mechanisms. By destroying the structural arrangement of mineral particles, the mechanisms of protection that are based on encapsulation will not be taken into account and a redistribution of organic matter onto mineral surfaces may occur. The use of chemical extraction techniques (e.g. alkaline reagents to extract humic materials) to examine the organic mater associated with soil minerals is also not recommended due to their inability to quantitatively extract organic materials.

In addition, each mechanism of protection can operate on one or more different components of the soil organic fraction. An attempt to delineate the organic

fractions acted on by the protection mechanisms discussed in this paper is given in Fig. 11. The magnitude of protection offered by each mechanism will play an important role in defining the chemical structure of the soil organic fraction by disrupting the natural progression of decomposition based on chemical recalcitrance of the organic matter.

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