δ^{13}C and δ^{15}N profiles in 14C-dated Oxisol and Vertisols as a function of soil chemistry and mineralogy

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Abstract

The analyses of stable isotope ratios of carbon (δ^{13}C) and nitrogen (δ^{15}N) of soil organic matter (SOM) is an increasingly used tool to estimate soil carbon turnover, to assess degree of soil development, and to study historical C3/C4 vegetation changes. However, the exact processes that control δ^{13}C- and δ^{15}N-enrichment of SOM within a soil profile are still not clearly identified. To better understand the isotopic processes associated with decomposition of SOM, we studied two Vertisol profiles and one Oxisol profile from southern Queensland by radiogenic (14C), stable isotopic (δ^{13}C, δ^{15}N), and spectroscopic (13C-NMR and FTIR) methods. The findings of this study demonstrate that fundamental differences exist in δ^{13}C and δ^{15}N fractionation dynamics in different soil types and that isotopic fractionation is highly influenced by soil chemistry, mineralogy, and type of organic matter input. Stable isotopic analyses of the Oxisol show the typically observed increase in δ^{13}C and δ^{15}N in the subsurface horizon whereas the Vertisols show consistently decreasing values with depth. The high degree of 13C-enrichment in the Oxisol compared with the Vertisols cannot be simply explained with increased fractionation due to soil age, as the 14C age of the Vertisols is greater and increases more rapidly with depth, compared with that of the Oxisol.

Data from 13C-NMR, XRF and IR data together with data on pH and clay content reveal a more complex picture of isotopic fractionation in soils. The Oxisol is dominated by O-alkyl carbon and aromatic material whereas the Vertisols contain higher amounts of alkyl carbon. Smectite and kaolinite are the dominant clay minerals in the Vertisols while the Oxisol is dominated by gibbsite, kaolinite, and Fe and Al-oxides.

We suggest that the 13C- and 15N-depletion in the Vertisols is associated with low pH, which inhibits nitrification and promotes stabilization of 13C-depleted alkyl material by smectitic clays. The 13C-enrichment in the Oxisol correlates with a high abundance of relatively 13C-enriched O-alkyl...
carbon, which is a mix of primary materials (plant carbohydrates) as well as secondary (microbially synthesized) carbon. The abundance of relatively labile O-alkyl carbon even at depth is likely due to physico-chemical protection through complexation with Fe- and Al-oxides.
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Keywords: $^{13}\text{C}$; $^{15}\text{N}$; Soil organic carbon; $^{13}\text{C}$-NMR; Vertisol

1. Introduction

The role of soil organic matter in the world’s climate has become the focus of recent studies, particularly with suggestions by the Kyoto protocol that soils may act as a potential sink for CO$_2$ (Lugo and Brown, 1993; Raich and Potter, 1995). With approximately 1500 Gt C contained in the upper meter of the world’s mineral soils (e.g. Batjes, 1996), changes in climate and land-use will have significant effects on the carbon budget, particularly with respect to the turnover rate of soil carbon. Therefore, the need to adequately assess size and turnover time of soil organic matter pools is essential to model global carbon dynamics as well as to implement any carbon accounting system. In order to achieve this goal, relatively inexpensive analytical methods, such as stable isotopic analyses, are often sought.

As a result, the application of stable carbon isotopic ($\delta^{13}\text{C}$) analyses (and to a lesser degree $\delta^{15}\text{N}$) to soil organic matter (SOM) studies has become an increasingly used tool to estimate soil carbon turnover (O’Brien and Stout, 1978; Balesdent et al., 1988, 1993; Balesdent and Mariotti, 1996; Bernoux et al., 1998), assess degree of decomposition (Stout and Rafter, 1978; Ladyman and Harkness, 1980; Nadelhoffer and Fry, 1988; Becker-Heidmann and Scharpenseel, 1992; Wedin et al., 1995; Ehleringer et al., 2000; Connin et al., 2001), and study historical C3/C4 vegetation changes (Boutton, 1996; Pessenda et al., 1996a,b; Boutton et al., 1993, 1998).

These applications are based on two fundamental assumptions (for more detail, see the excellent summaries by Boutton, 1996; Balesdent and Mariotti, 1996; Ehleringer et al., 2000):

1. The $\delta^{13}\text{C}$ value of SOM is assumed to increase by 1–3\% with depth due to one or more of the following processes;
   (a) The Suess effect ($^{13}\text{C}$-depletion in modern atmospheric carbon since industrialization),
   (b) $^{13}\text{C}$ fractionation by soil microorganisms during decomposition of SOM and addition of $^{13}\text{C}$-enriched microbial biomass,
   (c) Long-term changes in environmental stress factors (e.g. light intensity, water stress), which limit fractionation in the plant to conserve CO$_2$,
   (d) Translocation of relatively undecomposed ($^{13}\text{C}$-enriched) soluble carbon fractions downprofile.
2. The distinct isotopic difference ($\Delta^{13}\text{C}$) of C3 (average—26\%) and C4 (average—12\%) plant organic material is presumed to remain unchanged during decompositional processes (i.e. no difference in fractionation of C3 compared with C4 organic matter).
Fractionation dynamics of nitrogen in soils are commonly assumed to progress towards 15N-enrichment due to decomposition of SOM as the proportion of 15N-enriched microbial biomass increases (Nadelhoffer and Fry, 1994). Since most nitrogen in SOM exists in organic forms, this pool tends to dominate Δ15N values in the soil surface. However, inorganic nitrogen becomes important at depth where organic nitrogen contents decline. Δ15N values of soil inorganic nitrogen are controlled by nitrification reactions (resulting in 15N-enrichment of ammonium), denitrification (resulting in 15N-enrichment of nitrate), leaching of nitrate, and adsorption of ammonium on clays (Nadelhoffer and Fry, 1994; Kendall, 1998).

Δ13C analysis has been used to calculate definite percentages of C4 and C3 inputs into soil as well as into paleosol organic matter by inferring that Δ13C changes between 1‰ and 3‰ are due to soil-inherent processes and changes greater than 3‰ are due to a mixed input of C3 and C4 plants (e.g. Balesdent et al., 1987; Martin et al., 1990; Bernoux et al., 1998; Boutton et al., 1999; Sikes, 1994; Wang et al., 1997; Wang and Follmer, 1998). Similarly, Δ13C analysis has been used to estimate organic matter turnover rates after changes in vegetation (C3 vs. C4) (e.g. Andreux et al., 1990; Skjemstad et al., 1994b; Arrouays et al., 1995; Ågren et al., 1996; Bernoux et al., 1998; Scharpenseel and Pfeiffer, 1998). Δ13C studies of SOM can yield important information about turnover time of different soil fractions as well as past vegetation changes when used in conjunction with 14C dating, separation of soil organic matter into different carbon pools, and stable isotopic data of the plant biomass (e.g. Huang et al., 1996; Leavitt et al., 1996; Pessenda et al., 1996a,b).

However, caution should be used when trying to represent changes in Δ13C and Δ15N of SOM due to decompositional processes by universally applicable formulae as, for example, in the CENTURY (www.nrel.colostate.edu/projects/century), the NICCCE (van Dam and van Breemen, 1995), and the BIOME3.5 model (Buchmann and Kaplan, 2001), especially when Δ13C data of SOM are the only source of information. Because the chemical and mineralogical variability of soils influences the rate of decomposition and degree of isotopic fractionation of SOM, modelling Δ13C changes in soil is a complex exercise which none of the existing models addresses adequately. Buchmann and Kaplan (2001) reported that BIOME3.5 underestimated carbon isotopic discrimination by 3‰ (a carbon flux of 0.7 Gt C year−1) simply due to the heterogeneity of the soil.

The fact that the dynamics of isotopic fractionation of SOM are still not well understood (Ehleringer et al., 2000) is indicated by the following examples. The proportion of relatively 13C-depleted lignin (on average—4‰) has been reported to generally increase with degree of decomposition, which should lead to a decrease in Δ13C values. Conversely, most soils show 13C-enrichment with depth (Benner et al., 1987; Wedin et al., 1995; Boutton, 1996) and van Bergen et al. (1997, 1998) documented that while lignin makes up a significant fraction of the humic top soil, it markedly declines in the mineral soil.

Quantification of microbial fractionation of SOM has been attempted in culture experiments, but no compelling direct (in-situ) evidence for significant isotopic fractionation has yet been reported (Ehleringer et al., 2000; Huang et al., 1997). Results from litter bag studies, aimed to simulate changes in Δ13C during decom-
position, often do not report significant changes in the isotopic value despite a considerable decrease in carbon mass (Melillo et al., 1989; Huang et al., 1997; Connin et al., 2001). A $\delta^{13}$C increase of over 5% has been reported in an Ultisol profile from a tropical forest of Kenya (Krull et al., 2002). This large isotopic fractionation with depth cannot be explained by a recent vegetation change from C4 grasses to C3 rainforest since the forest in its current condition is considered a “living remnant” of the Pleistocene period. These examples document that carbon isotopic dynamics do not follow a simple pattern, but rather the extent of isotopic fractionation seems to be influenced by a combination of environmental, chemical, and mineralogical conditions. Factors that may influence fractionation dynamics such as complexation of organic matter with Fe and Al, adsorption of organic matter on clay surfaces, and the effect of decomposition on individual chemical constituents of SOM, as revealed by $^{13}$C-NMR studies, have been rarely considered in combination with stable isotopic studies. Notable exceptions that use a combination of techniques are studies by Becker-Heidmann and Scharppenseel (1986), Spiker and Hatcher (1987), Macko et al. (1991), Veldkamp (1994), Golchin et al. (1995), Augris et al. (1998), Lichtfouse et al. (1998) and Skjemstad et al. (2001).

The aim of this study was to link data from $^{13}$C-NMR analyses, mid-infrared analyses, major element composition and radiogenic ($^{14}$C) isotopes with $\delta^{13}$C and $\delta^{15}$N changes in SOM with increasing soil depth of two different soil types.

### 2. Materials and methods

#### 2.1. Soils

Archived soil samples of three soil profiles (two Vertisols and one Oxisol) from southern Queensland, previously collected by G.D. Hubble, were used for this study. Samples were taken from a single core at each location, extending from the surface to weathered parent material. The location of the soils is shown in Fig. 1. Vertisols are widespread soils throughout Australia, extending from south-eastern South Australia to the Northern Territories. They occur predominantly on broad riverine plains, which are influenced by both alluvial and colluvial processes (Stace et al., 1968). Most Vertisols are alkaline, except for those associated with brigalow (Acacia harpophylla) forests, which tend to be acidic throughout (Stace et al., 1968).

The Chinchilla (CHI) Vertisol (Chromustert) is located on a gently undulating plain in the Chinchilla district (26°43’S; 150°36’E) and is characterized by melon-hole gilgai relief (Stace et al., 1968). The deeply weathered profile extends to a depth of 375 cm and its parent material consists of fine sand- and siltstones of the Mesozoic Kumbarilla beds. The mean annual rainfall is 635 mm (summer maximum). The original virgin forest of brigalow, belah, wilga and tea-tree has been cleared and consists now of whip-stick regrowth of brigalow (A. harpophylla), belah (Casuarina cristata), few bottle trees (Brachychiton rupestris) and tree pear (Opuntia tomentosa). The partial ground cover consists of herbaceous and gramineous plants such as brigalow burr (Bassia tetracuspis), creeping saltbush (Atriplex semibaccata), brigalow grass (Paspalidium caespitosum) and
roly poly (*Salsola kali*) (Stace et al., 1968). Drainage of both Vertisols is very slow (Stace et al., 1968).

The deeply weathered Paget Creek (PG) Vertisol (Chromustert) is located west of Dalby (27°27’S; 150°31’E) and has formed on the lower edge of a gently sloping pediment of lower Cretaceous sand- and mudstones. The profile extends to a depth of 375 cm, below which there is a broad transition to weathered material to 480 cm (Hubble, unpublished data). Annual rainfall averages 570 mm (summer maximum) and the vegetation consists of roadside remnant brigalow of up to 22-m-tall adjacent to pastures.

Oxisols occur throughout the subhumid to humid areas of eastern Australia. Most of these soil types are associated with well-drained sites on hilly uplands and plateaus (Stace et al., 1968). The 250 cm deep profile of the Beechmont (BE) Oxisol, south of Brisbane (28°10’S; 153°12’E), is located on a gently sloping plateau of Tertiary basaltic material (Hubble, unpublished data). Mean annual rainfall is 1500 mm (summer maximum) and the vegetation consists of open forest of different eucalypt species (mainly *Eucalyptus eugenioides*, *Eucalyptus biturbinata*, *Eucalyptus melliodora*) and *Allocasuarina torulosa*.

2.2. Isotopic analyses

Analyses for natural $^{14}$C abundance of these soils in 10- to 20-cm intervals was previously carried out by Dr. A.W. Scharpenseel, University of Hamburg, Germany.
Natural $^{14}$C concentrations were determined as described by Becker-Heidmann (1989) by combustion and conversion of organic carbon to strontium carbonate, benzene synthesis and measurement by liquid scintillation spectrometry. The $^{14}$C activity was measured for 2800 min on a Packard Tri Carb Model 3320 and on a Berthold Betaszint BF 5000 in 20-min intervals. Correction and error analyses were done by software developed by Schiffmann and Becker-Heidmann (unpublished). Background and NBS standard were counted for 5000 min (Becker-Heidmann and Scharpenseel, 1986).

For stable isotopic analyses, 10–50 mg of sample was placed into ultra-clean tin capsules and sealed. Samples were combusted and analysed on a 20–20 Europa Scientific Automated Nitrogen Carbon Analysis-Mass Spectrometer (ANCA-MS). The reaction products from combustion were separated by gas chromatography to give pulses of N$_2$ and CO$_2$ for analysis of total carbon (TOC) and nitrogen (TN) content as well as $\delta^{13}$C and $\delta^{15}$N values. The average error from replicates was 0.22 $\%_\circ$ for $\delta^{13}$C and 0.42 $\%_\circ$ for $\delta^{15}$N. Isotope results are reported in the conventional $\delta$ notation as per mil deviation from the PDB and N$_{air}$ standards (Peterson and Fry, 1987).

2.3. $^{13}$C nuclear magnetic resonance spectroscopy

Prior to nuclear magnetic resonance NMR spectroscopy, bulk soil samples were treated with 2% hydrofluoric acid (HF) to decrease the amount of paramagnetic material and to increase the organic matter content (Skjemstad et al., 1994a). Sample material was spun at 5 kHz in 7-mm diameter zirconia rotors with Kel-F caps. The $^{13}$C cross-polarization with magic angle spinning (CP/MAS) NMR spectra were obtained at 50.309 MHz on a Varian Unity 200 spectrometer with a 4.7-T wide-bore Oxford superconducting magnet using a 7-mm Doty Scientific MAS probe. A contact time of 1 ms was used, and a recycle delay time of 0.3 s was used to ensure complete relaxation between scans (recycle delay>7 T$_1$,H) (Wilson, 1987). The spectra were plotted between −100 and 300 ppm using a Lorentzian line broadening of 50 kHz. The NMR spectra were divided into five chemical shift regions, representing alkyl C (0–46 ppm), O-alkyl C (46–110 ppm), aromatic C (divided into aryl C (110–145 ppm) and O-aryl C (145–165 ppm), carbonyl C (165–190 ppm) and aldehyde/ketone C (190–220 ppm). The relative proportional contributions of each carbon type were determined by integration of each spectrum over given chemical shift ranges.

2.4. Scanning electron microscopy

Scanning electron microscopy (SEM) was carried out on a Cambridge Stereoscan S250 on samples coated with 20 nm of carbon. Elementary characterization was performed using a Link AN1000 EDX analyser.

2.5. DRIFT spectroscopy and PLS analysis

Infrared spectra were collected on a rapid-scan Bio-Rad FTS-175™ FTIR spectrometer equipped with a Peltier-cooled DTGS detector and extended range KBr beam-splitter,
scanning at 8 cm\(^{-1}\) resolution and a 0.5-s scan rate to give a spectral range of 8000–470 cm\(^{-1}\). The instrument compartment and sample chamber were purged with H\(_2\)O- and CO\(_2\)-free air to remove atmospheric effects. Sampling was by diffuse reflectance from the neat powdered sample surface using an off-axis diffuse reflectance accessory (HarrickTM DRS-3SO).

Powdered samples were poured into 10 mm diameter stainless steel cups and the top surfaces levelled. Spectra were recorded for infrared measurements from 4000 to 500 cm\(^{-1}\) at 1.92 cm\(^{-1}\) intervals and a resolution of 4 cm\(^{-1}\). The spectral operating software, WIN_IR™ Ver. 4.0, a variant of the Galactic™ (NH) GRAMS-32™ operating system, was provided as the standard operating system for the FTS-175 spectrometer. The partial least squares (PLS) method was based on algorithms published by Haaland and Thomas (1988) and incorporated into PLSplus/IQ© Ver. 3.0.

Janik et al. (1995, 1998) demonstrated that by application of partial least square (PLS) analysis, mid-infrared diffuse reflectance Fourier transform (DRIFT) spectra can be used to model soil properties. Infrared spectroscopy, coupled with the PLS analysis, has been successfully used for soil chemical analysis due to its sensitivity to both the organic and inorganic phases. It therefore constitutes a fast and economical alternative to standard X-ray and wet-chemical analyses (Janik et al., 1995, 1998). A more detailed description of the methodology and calibration sets for prediction of XRF data in soils can be found in Janik et al. (1995).

2.6. NO\(_3^-\) and NH\(_4^+\) contents

Concentrations of NO\(_3^-\) and NH\(_4^+\) were determined using the methods described by Rayment and Higginson (1992). Two grams of soil were extracted with 10 ml of 2 M KCl for 1 h, filtered, and analyzed by segmented flow analysis. Analysis of NO\(_3^-\) was by Cd reduction and colour development with sulphanilimide/NEDD. NH\(_4^+\) was analyzed using gas diffusion and colour development with salicylate/sodium nitroprusside and DCIC. We used an Alpkem ‘Flow Solution’ segmented flow analyser comprising 501 sampler, 502 pump and 503 cartridge heater with ‘Flow Solution IV’ ER detectors operating at 640 nm for NH\(_4^+\) and at 540 nm for NO\(_3^-\). WinFLOW v3 software was used to collect data and calculate results.

3. Results

3.1. Clay content and soil pH

Analyses of clay content and soil pH values were compiled by the CSIRO Division of Soils and data are summarized in Table 1 (Stace et al., 1968; Hubble, unpublished data). The Vertisols are characterized by relatively high clay content (average 64.0% in CHI and 67.6% in PG) and low soil pH (ranging from 6.5 to 4.4 in CHI and from 5.7 to 4.1 in PG) throughout the profiles (Table 1). The Oxisol shows a distinct clay-enriched horizon where clay content increases from 64% at the surface to 87% at 110 cm. Soil pH values in BE decrease with depth and range from 6.3 to 4.8 (Table 1).
Table 1
Depth distribution of $^{14}$C, total organic carbon (TOC), total nitrogen (TN), $\text{NH}_4^+$ (as % of TN), $\text{NO}_3^-/\text{CO}_2$ (as % of TN), N$_{\text{org}}$ (as % of TN), pH, and clay content for Chinchilla (CHI), Paget Creek (PG) and Beechmont (BE)

<table>
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<th>Depth (cm)</th>
<th>$^{14}$C (years B.P.)</th>
<th>$^{14}$C error (± years)</th>
<th>TOC (%)</th>
<th>TN (%)</th>
<th>$\text{NO}_3^-$/CO$_2$ (±%TN)</th>
<th>$\text{NH}_4^+$ (±%TN)</th>
<th>N$_{\text{org}}$ (±%TN)</th>
<th>pH</th>
<th>Clay content (%)</th>
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Isotopic and elemental data for the three soil profiles are summarized in Table 1 and Figs. 2–4. Both Vertisols have similar average $^{13}\text{C}$ values with Chinchilla (CHI) averaging $\delta^{13}\text{C}=-25.5 \pm 0.40\%$e and Paget Creek (PG) averaging $-24.3 \pm 0.36\%e$. Both soils show a net isotopic difference ($\Delta^{13}\text{C}=\delta^{13}\text{C}_{\text{max}}-\delta^{13}\text{C}_{\text{min}}$) of $-2.2\%e$ and decreasing $\delta^{13}\text{C}$ values with depth (Figs 2A and 3A). TOC and TN contents decrease with depth, with most of the loss occurring in the uppermost 50 cm. Here, TOC contents decrease by 74% (from 2.6% to 0.6%) and TN contents decrease by 35% (from 0.23% to 0.08%) (Table 1).

$\delta^{15}\text{N}$ values average $-1.4 \pm 1.06\%e$ ($\Delta^{15}\text{N}=8.7\%e$) for CHI and $+1.0 \pm 0.25\%e$ ($\Delta^{15}\text{N}=6.1\%e$) for PG. In CHI, $\delta^{15}\text{N}$ values approximately follow the $\delta^{13}\text{C}$ curve to a depth of 145 cm ($R^2=0.66$) (Fig. 2B). In PG, a similar co-variation (decreasing values) between $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ is observed to a depth of 60 cm ($R^2=0.50$) (Fig. 3B). C/N ratios are commonly used as an indicator of decomposition and tend to decrease with increased decomposition. For calculation of this ratio, it is important to use the organic N ($N_{\text{org}}$)

### Table 1 (continued)

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### 3.2. $\delta^{13}\text{C}$, TOC, $\delta^{15}\text{N}$, TN and $^{14}\text{C}$ analyses

Isotopic and elemental data for the three soil profiles are summarized in Table 1 and Figs. 2–4. Both Vertisols have similar average $\delta^{13}\text{C}$ values with Chinchilla (CHI) averaging $-25.5 \pm 0.40\%e$ and Paget Creek (PG) averaging $-24.3 \pm 0.36\%e$. Both soils show a net isotopic difference ($\Delta^{13}\text{C}=\delta^{13}\text{C}_{\text{max}}-\delta^{13}\text{C}_{\text{min}}$) of $-2.2\%e$ and decreasing $\delta^{13}\text{C}$ values with depth (Figs 2A and 3A). TOC and TN contents decrease with depth, with most of the loss occurring in the uppermost 50 cm. Here, TOC contents decrease by 74% (from 2.6% to 0.6%) and TN contents decrease by 35% (from 0.23% to 0.08%) (Table 1).

$\delta^{15}\text{N}$ values average $-1.4 \pm 1.06\%e$ ($\Delta^{15}\text{N}=8.7\%e$) for CHI and $+1.0 \pm 0.25\%e$ ($\Delta^{15}\text{N}=6.1\%e$) for PG. In CHI, $\delta^{15}\text{N}$ values approximately follow the $\delta^{13}\text{C}$ curve to a depth of 145 cm ($R^2=0.66$) (Fig. 2B). In PG, a similar co-variation (decreasing values) between $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ is observed to a depth of 60 cm ($R^2=0.50$) (Fig. 3B). C/N ratios are commonly used as an indicator of decomposition and tend to decrease with increased decomposition. For calculation of this ratio, it is important to use the organic N ($N_{\text{org}}$)
contents instead of the total N contents, as inorganic N can make up a significant fraction with depth (Meyers, 1997). C/N_{org} ratios for both soils steadily decrease from a ratio of 12 at the surface to a ratio of 4 and 5 at depth for the CHI and PG soils (Figs. 2C and 3C).

Radiocarbon age dates for CHI show contribution from modern bomb carbon (less than 50 years) in the uppermost 30 cm and age rapidly increases below, except for a

Fig. 2. Chinchilla (CHI) Vertisol depth profiles of (A) \( \delta^{13}C \) from SOM, (B) \( \delta^{15}N \) from SOM, (C) C/N_{org} ratios and (D) \(^{14}C \) age dates.

Fig. 3. Paget Creek (PG) Vertisol depth profiles of (A) \( \delta^{13}C \) from SOM, (B) \( \delta^{15}N \) from SOM, (C) C/N ratios and (D) \(^{14}C \) age dates.
sharp inflection between 85 and 115 cm (Table 1, Fig. 2D). In PG modern carbon occurs in the uppermost 20 cm, below which $^{14}$C age increases with depth to 11,570 ($\pm$ 210) years (Table 1, Fig. 3D). Three rapid increases in soil age are associated with short reversals in $^{14}$C age. These “steps” occur between 105–115 cm, 125–155 cm and 165–185 cm (Fig. 3D).

The average $\delta^{13}$C value for the Beechmont Oxisol (BE) is $-25.1 \pm 0.53\%$ ($\Delta^{13}$C = 3.0$\%$). $\delta^{13}$C values rapidly increase in the uppermost 25 cm and remain relatively $^{13}$C-enriched to a depth of 110 cm (Fig. 4A). TOC contents decrease by 18% in the uppermost 50 cm (from 8.2% to 1.5%) and continue to steadily decrease thereafter (Table 1).

Average $\delta^{15}$N values for BE are $+0.8 \pm 1.1\%$ ($\Delta^{15}$N = 16.3$\%$). $\delta^{15}$N values follow the $\delta^{13}$C trend of increasing values in the uppermost 25 cm (average $R^2 = 0.9$) (Fig. 4B). Below that depth $\delta^{15}$N values vary highly and it is difficult to depict a significant trend. C/N$_{org}$ ratios in BE are 11.3 at the surface, then decrease to 9.6 at 15 cm and steadily increase thereafter to 15 (Fig. 4C).

Contribution from modern carbon occurs in the uppermost 20 cm of BE (Table 1, Fig. 4D). Below 20 cm, the $^{14}$C profile from BE shows relatively young soil carbon (average: 273 $\pm$ 60 years) until a depth of 50 cm, from whereon soil age rapidly increases to 2020 years at 90 cm (Fig. 4D).

3.3. $^{13}$C-NMR analyses

Fig. 5 shows the solid-state CP/MAS $^{13}$C-NMR spectra acquired from bulk soil organic matter from all soils. The distribution of each carbon type, as determined by integration of the spectral areas, is summarized in Table 2. Peak assignments were performed with data
from the literature (e.g. Kögel et al., 1988; Golchin et al., 1994; Kögel-Knabner, 1997; Skjemstad et al., 1997).

Major resonances in the soil profiles show varying proportions of peaks centred around 30, 55, 72, 105, 130, 152 and 172 ppm. In the alkyl range (0–50 ppm), the signal between 29 and 33 ppm is typical for methylene carbons, commonly derived from long-chained lipids and aliphatic biopolymers, such as suberin, cutin and resin (Skjemstad et al., 1983; Oades, 1995; Kögel-Knabner, 1997). Resonances in the O-alkyl region at 55 ppm arise from α-C to N in proteinaceous structures and also from O-methyl C. Secondary alcohols resonate at 72 ppm and dioxygenated (anomeric) polysaccharides at 105 ppm. In SOM, these structures originate most likely from
carbohydrates, e.g. cellulose (Skjemstad et al., 1998). Peaks at 129 and 152 ppm fall in the aromatic (aryl and O-aryl carbon) region and represent aromatic and unsaturated structures such as lignin, tannins and charcoal (Skjemstad and Dalal, 1987; Skjemstad et al., 1996). Resonances in the carbonyl region (165–220 ppm) have been attributed to amides, carboxylic acids and esters.

The \( ^{13}C \)-NMR spectra of both Vertisols are characterized by relatively high amounts of alkyl carbon throughout the soil profile (Fig. 5A,B; Table 2). Abundance of O-alkyl and carbonyl groups decrease with depth, whereas the relative proportion of aromatic carbon increases. By comparison, \( ^{13}C \)-NMR spectra of the Oxisol show predominance of O-alkyl and aromatic carbon (Fig. 5C; Table 2).

3.4. Mid-infrared analyses

Mid-infrared spectra were used to obtain a qualitative estimate of clay mineralogy. To test whether significant changes in clay mineralogy occurred within the profiles, samples were analysed from three different depths. Interpretation of spectra was based on published
spectra by van der Marel and Beutelspacher (1976) and representative spectra of each soil are shown in Fig. 6. The spectra of the Vertisols (CHI and PG) are very similar at all depths, characterized by high abundance of kaolinite and smectite (Fig. 6A,B). The spectra of the BE Oxisol are characterized by a mixture of kaolinite, gibbsite (hydrargillite) and hematite (Fig. 6C) and kaolinite and goethite become more abundant with depth (data not shown).

3.5. FTIR-predicted XRF data

Data from partial least square (PLS) analysis, mid-infrared diffuse reflectance Fourier transform (DRIFT) spectra for SiO$_2$, Al$_2$O$_3$ and Fe$_2$O$_3$ are illustrated in Fig. 7. Both Vertisol profiles are characterized by high SiO$_2$ contents throughout the profiles with CHI averaging 73.8 wt.% and PG averaging 61.7 wt.%. Al$_2$O$_3$ contents average 15.2 wt.% in CHI and 19.6 wt.% in PG and contents tend to increase with depth (Fig. 7A,B). Fe$_2$O$_3$ contents decrease with depth in CHI from 4.7 to around 2.5 wt.% (average 2.9 wt.%) and are relatively constant for PG, averaging 4.9 wt.% (Fig. 7A,B).

The BE Oxisol shows a decrease in SiO$_2$ contents from 33.6 to 28.6 wt.% (average 29.4 wt.%) and Al$_2$O$_3$ contents increase from 19.3 to 25.4 wt.% (average 25.0 wt.%) (Fig. 7C). Fe$_2$O$_3$ contents are high, averaging 22.5 wt.% and increase with depth from 15.3 to 29.9 wt.% at 170 cm, then decrease to 24.2 wt.% at 230 cm (Fig. 7C).
Fig. 6. Mid-FTIR DRIFT spectra of representative soil samples of (A) the Chinchilla (CHI) Vertisol, (B) the Paget Creek (PG) Vertisol and (C) the Beechmont (BE) Oxisol.
3.6. NO$_3^-$ and NH$_4^+$ contents

Changes in inorganic nitrogen species with depth are included in Table 1. The inorganic nitrogen ($N_{\text{inorg}}$) pool in all soils is dominated by NH$_4^+$ whereas NO$_3^-$ constitutes only a minor component (Table 1). Both Vertisols show a rapid increase in $N_{\text{inorg}}$ in the uppermost 50 cm from 6.5% of TN to a maximum of 32.0% of TN in CHI and from 8.2% to 18.9% of TN in PG. Contents of $N_{\text{inorg}}$ in the Oxisol show an abrupt increase below 35 cm from 4% of TN to 33.3% of TN (Table 1).

4. Discussion

4.1. Vertisols

Vertisols are clay soils (>35% clay) with shrink-swell properties and are characterized by cracking during dry periods. Cracks are at least 5 mm wide and extend to either the plough layer or the base of the self-mulching horizon (Isbell, 1998). Because of its self-mulching quality and formation of cracks, vertical translocation of younger ($^{14}$C-rich) carbon is commonly observed in Vertisols (Scharpenseel et al., 1986, 1989). Self-mulching can even lead to a partial “inversion” of the soil, hence the term “invert” to characterize this soil order (Brady, 1990).

The $^{14}$C ages in CHI and PG show contribution of modern carbon to a depth of 20–30 cm, supporting the concept of self-mulching and bioturbation, typical for the uppermost 30
cm of Vertisols (Figs. 2D and 3D). This input of young, relatively undecomposed and labile carbon to the surface and translocation to subsurface layers is supported by $^{13}$C-NMR spectra in this interval, which show abundant alkyl, $O$-alkyl, carbonyl and amide carbon, indicating presence of polymethylene (lipid-type material), polysaccharides (e.g. cellulose), proteins and carboxylic acids (Fig. 5A,B; Table 2). In CHI, the abundance of relatively labile $O$-alkyl carbon increases in the 20–30 cm interval, which coincides with a strong pulse in modern, $^{14}$C-rich C (Tables 1 and 2). These trends suggest that self-mulching processes, solubilized C from the surface and root-derived carbon contributed both labile ($O$-alkyl and proteinaceous) and relatively young material to these subsurface soil layers. In addition, the $C/N_{org}$ ratios of CHI and PG in the surface interval are between 11 and 12, confirming that SOM is dominated by a relatively fresh and undecomposed fraction at 30 cm depth (Table 1, Figs. 2C and 3C).

Despite the relatively fresh chemical composition of SOM in the uppermost 30 cm, the distributions of $\delta^{13}$C and $\delta^{15}$N with depth neither show relatively constant isotopic values (as one would expect in the case of integration of $^{14}$C-rich material into lower layers) nor do they show increasing values with depth (as often observed in soils and attributed to microbial decomposition or the Suess effect). Instead, both $\delta^{13}$C and $\delta^{15}$N show a trend towards more depleted values, which extends below the uppermost 30 cm and continues with depth (Figs. 2A,B and 3A,B). At depths below 30 cm, SOM is characterized by both a greater degree of decomposition (decreasing $C/N_{org}$ ratios, decrease in $O$-alkyl carbon) and greater age (increasing $^{14}$C age). In PG, the abrupt increase in $^{14}$C ages at 150 cm is probably related to a hiatus in soil formation, erosion, and subsequent deposition of younger material (Fig. 3A,D). Interestingly, there is a concomitant abrupt change in $\delta^{13}$C by almost $-2\%$, which could be related to changes in paleoclimate during the 55,000- to 7000-year interval. This is supported by studies indicating a precipitation maximum around this period and drier conditions thereafter in much of southern and eastern Australia (Shulmeister and Lees, 1995; Shulmeister, 1999). Although the change from a precipitation maximum to drier conditions was accompanied by a change in vegetation (Shulmeister and Lees, 1995), the $^{13}$C-depleted values are probably the result of less water-stressed conditions during the precipitation maximum compared with drier conditions thereafter. Water stress in C3 plants has been shown to result in less fractionation and consequently slightly $^{13}$C-enriched values (Ehleringer and Cooper, 1988; Stewart et al., 1995).

However, the observation of overall decreasing $\delta^{13}$C and $\delta^{15}$N values in these Vertisols, despite increased degree of decomposition, is of crucial importance, since in absence of long-term vegetation changes, $\delta^{13}$C and $\delta^{15}$N values of SOM are assumed to increase with depth. Since the premise of increasing values with depth is often taken as a set parameter and constitutes the basis for soil carbon models, the decreasing isotopic trends in these Vertisols indicate that fractionation processes can be more complex and call for critical investigation of the responsible fractionation mechanisms. In the following we will discuss possible mechanisms that could explain these unconventional trends.

4.1.1. Decreased C4 input

Clearing of virgin forest occurred within the last 50 years at the CHI site and adjacent to the PG site, resulting in Acacia whipstick regrowth at CHI and open pastures adjacent to
the tall brigalow remnant at PG. Whereas dense virgin stands of *Acacia* forests are often characterized by bare soil, tree clearing results in greater availability of light and water and allowing for invasion of herbaceous and gramineous species. Therefore, the relatively enriched value of $-24\%e$ in the surface horizon of CHI and PG (compared with the average $\delta^{13}C$ values of *Acacia* species of $-27.1\%e$; compiled from Schulze et al., 1991, 1998; Stewart et al., 1995; Arens et al., 2000) could be due to a more substantial ground cover of C4 species after clearing of virgin forest. This C4 contribution is likely to be limited to the $^{14}C$-rich uppermost (20–30 cm) layers of the soil profile, as widespread land-clearing in Australia began no earlier than 100 years ago. Below 30 cm depth, SOM is likely to be almost entirely C3-derived, as virgin stands of *Acacia* usually preclude colonization by grasses due to competition for water and canopy shading. This interpretation can account for the decrease in $\delta^{13}C$ in the uppermost 30 cm but it also falls short of explaining the continued decrease of $\delta^{13}C$ with depth. It also falls short to explain the $\delta^{15}N$ depletion, because $\delta^{15}N$ values do not differ between C3 and C4 vegetation (Heaton, 1987; Mordelet et al., 1996; Turekian et al., 1998) and since both $\delta^{13}C$ and $\delta^{15}N$ show the decreasing values with depth, factors other than vegetation change must be contributing to the $^{13}C$- and $^{15}N$-depletion.

4.1.2. Low pH

Both Vertisols are characterized by low pH values and a trend towards more acidic conditions with depth (Table 1). Low pH promotes hydrolytic reactions in soil and acid hydrolysis is known to remove proteins, nucleic acids and polysaccharides (Schnitzer and Khan, 1972; Smith, 1987; Ostle et al., 1999; Zang et al., 2000), all of which are enriched in $^{13}C$ and in the case of proteins, enriched in $^{15}N$ as well (Macko et al., 1986; Ostle et al., 1999). Similarly, Stout and Rafter (1978) reported that $\delta^{13}C$ values in peats decreased with depth which they attributed to hydrolytic removal of labile and acid-soluble SOM fractions, resulting in the retention of $^{13}C$-depleted lignin. Accordingly, $^{13}C$-NMR spectra of the CHI and PG Vertisols would be expected to show a sharp decline in $^{13}C$-enriched O-alkyl carbon in the uppermost 20 cm and a gradual decline thereafter. However, while PG shows a decline in O-alkyl C in the uppermost 30 cm, O-alkyl remains stable thereafter and the O-alkyl trends in CHI do not co-vary with the $\delta^{13}C$ trends (Table 2).

$\delta^{15}N$ values pose an additional difficulty since they represent a combination of fractionation of inorganic ($NO_3^-$ and $NH_4^+$) and organic N and therefore $\delta^{15}N$ values need to be discussed with respect to these two N species. In the surface horizon, where pH and carbon availability is still high (Table 1), $\delta^{15}N$ values of both Vertisols are $^{15}N$-enriched compared to an average $\delta^{15}N$ of $-0.4\%e$ measured for *Acacia* spp. (Mordelet et al., 1996). Since N contents in the surface soil are dominated by organic nitrogen (around 93% of TN; Table 1), this $^{15}N$-enrichment is most likely due to processes occurring in the organic fraction. The $^{15}N$-enrichment in the soil organic N compared with the precursor plant material is likely due to microbial fractionation, resulting in a shift towards a greater proportion of $^{15}N$-enriched microbial biomass. Although inorganic N constitutes a small amount in the surface soil, $^{15}N$-enrichment of the inorganic fraction is also likely to occur during nitrification (enrichment of $NH_3$) and denitrification (enrichment of $NO_3^-$) reactions (Handley and Raven, 1992; Nadelhoffer and Fry, 1994).
The pronounced decrease in $\delta^{15}N$ below 30 cm corresponds with a decrease in pH < 5. Here, TN values are low and inorganic N (N$_{\text{inorg}}$) contents increase relative to organic N (N$_{\text{org}}$). In fact, there appears to be a relationship between the declining N$_{\text{org}}$ contents and the decreasing $\delta^{15}N$ values. However, in the case of CHI, if the 6‰ shift from 4.8‰ at the surface to −1.2‰ at depth were just due to the changed proportions of inorganic to organic nitrogen, the N$_{\text{inorg}}$ pool would have been depleted by about −20‰, given that it comprises only 26% of the TN. Such a large fractionation in the natural environment is unlikely (Kendall, 1998) and it is not viable to assume such a process here. Instead, pH-related processes may contribute to the $^{15}$N-depletion. Low pH in the subsurface can hydrolyse $^{15}$N-enriched proteins, which may be leached out of the profile, leaving the remaining N$_{\text{org}}$ fraction depleted. However, this process assumes that these fractions are leached before they can be incorporated into microbial biomass. A potential explanation is that mineralization rate is slowed in these deeper, more acidic and slowly draining parts of the soil and that undecomposed, $^{15}$N-depleted root-derived material contributes to the N$_{\text{org}}$ pool. More importantly, under these low pH conditions and low carbon availability, nitrification is impeded and NH$_4^+$ remains $^{15}$N-depleted due to lack of fractionation (Brock et al., 1994). The source of $^{15}$N-depleted inorganic N is likely to be either from atmospheric deposition, where $\delta^{15}N_{\text{inorg}}$ may vary from −1‰ to −12‰, or from biological N fixation (Yoneyama, 1996). Nitrogen fixation imparts little fractionation and biologically fixed N averages −1.1‰ (Yoneyama, 1996). Furthermore, clays are known to readily stabilize NH$_4^+$ and $^{15}$N-depleted NH$_4^+$ may accumulate in the soil profile (Delwiche and Steyn, 1970).

Interestingly, N$_{\text{inorg}}$ contents in PG do not increase to the same extent as seen in CHI, and are only about half the amount (13% TN) of those at comparable depths in CHI (Table 1). Similarly, $\delta^{15}N$ values in PG decrease only by about 2.7‰ compared with 6‰ in the uppermost 100 cm in CHI (Fig. 2b). The larger decrease in $\delta^{15}N$ and greater amount of inorganic (NH$_4^+$) N in CHI compared with PG suggests that the degree of $^{15}$N-depletion at depth is likely to be controlled by the amount of depleted-NH$_4^+$ rather than by depleted, root-derived N$_{\text{org}}$.

4.1.3. Selective preservation of C fractions

As already pointed out in the discussion of soil pH, soil organic matter is composed of different fractions that vary in their isotopic composition. We applied solid state $^{13}$C-NMR to differentiate organic C on the basis of its chemistry and to evaluate changes in chemistry with respect to changes in isotopic trend. Fig. 8 shows the relative depletion or enrichment of biochemical fractions relative to the bulk plant material. $^{13}$C-NMR spectra of PG and particularly CHI show a stability and abundance of alkyl and aromatic carbon (Fig. 5A,B; Table 2). Skjemstad and Dalal (1987) and Skjemstad et al. (1986) reported a similar dominance of alkyl material in $^{13}$C-NMR and IR studies of SOM from Vertisol profiles. They found a close association (either chemically or physically) between alkyl carbon and clay material and concluded that this association probably accounted for the stability of alkyl carbon in these clay-rich soils. In particular, smectitic clays, as found in these Vertisols (Fig. 6A,B), are reported to have a greater potential for stabilization of SOM than other types of clay (Ransom et al., 1998). This observation is supported by Leinweber et al. (1999) who reported abundant clay-associated alkyl material in Vertisols. Leinweber et
al. (1999) further showed that Vertisols are characterized by abundant organo-mineral complexes and suggested that the robust binding between clays and specific types of organic matter indicated protective stabilization. Augris et al. (1998) and Lichtfouse et al. (1998, 1995A,B) reported abundant occurrence of non-hydrolysable, aliphatic (alkyl) macromolecules in acid, loamy forest soils. Similarly, van Bergen et al. (1998) and Bull et al. (2000a,b) observed in studies of soils from the Rothamsted classical experiments that 13C-depleted fractions such as lipids and lignin-derived (aromatic) were significantly higher in soils with low pH. Therefore, low pH and high clay content seem to promote stabilization of either primary (plant-derived) or secondary (microbially-derived) 13C-depleted alkyl and aromatic material. This stabilization may be achieved through formation of clay aggregates as Gates et al. (1998) found that microbial-derived organic matter caused aggregation of smectitic clays in Vertisols and so aided in protection of SOM.

Interestingly, 13C-NMR spectra also show that with increasing depth, alkyl material decreases and aromatic carbon becomes the dominant fraction, particularly in PG (Fig. 5A,B; Table 2). Resonances in the aromatic region are most likely due to lignin-derived carbon or charcoal, which are both considered highly recalcitrant. Lignin carbon is on average 3% 13C-depleted compared to bulk plant material (Fig. 8) whereas wood charcoal retains its isotopic signature (Pessenda et al., 1996a,b; Bird and Gröcke, 1997; Krull et al., unpublished data). The presence of charcoal in PG has been confirmed by scanning electron microscopic investigation, which shows finely divided angular particles with cellular morphology, which have been reported to be characteristic of charcoal (Fig. 9A–C) (Skjemstad et al., 1996; Schmidt et al., 1999). Whether the significant shift below 150 cm in PG towards more 13C-depleted values (Fig. 2B) is due to the greater proportion of aromatic (charcoal?) carbon or is due to a significant environmental change, remains to be investigated.
4.2. Oxisol

Oxisols are highly weathered soils and are characterized by a clay-rich subsurface horizon, dominated by hydrous oxides of iron and aluminium (Brady, 1990). Due to intense weathering and leaching processes, much of the silica in silicate-bearing minerals has been removed and hydrous oxides and kaolinitic clays dominate the soil mineralogy. The BE Oxisol is characterized by high amounts of kaolinite and gibbsite, low SiO$_2$ but high Al$_2$O$_3$ contents. Compared with the Vertisols, Fe$_2$O$_3$ contents are very high and increase with depth (Figs. 6C and 7C). Oxisols commonly occupy old land surfaces and are freely drained.

The BE Oxisol is characterized by a significant contribution from modern carbon within the uppermost 20 cm (Fig. 4D), probably derived from rhizosphere carbon, bioturbation and from translocation of soluble organic material (Zech et al., 1997). However, between 20 and 50 cm $^{14}$C age does not increase as quickly as in the Vertisols, but remains in the hundreds of years range. Although some authors argue that carbon from roots might contribute to this relatively stagnant $^{14}$C trend, it is possible that the source of

![Fig. 9. Electron micrographs of fragments of charred organic carbon (marked with an arrow) from the Paget Creek (PG) Vertisol after HF treatment. Charcoal is easily discernible due to its cellular morphology and sharp, angular boundaries, which distinguishes it from original plant material. Samples originate from (A) 60–70 cm, (B) 190–200 cm and (C) 260–270 cm depths. Scale bar: 20 μm.](image-url)
“young” carbon is organic matter that has escaped decomposition either by protection in microaggregates or due to chemical recalcitrance, such as in charcoal from recent fires (Baldock and Skjemstad, 2000; Krull et al., 2001). Within the 0–50 cm interval, $\delta^{13}C$ values show the often-cited trend towards increasing values (Fig. 4A). Below 50 cm $^{14}C$ age rapidly increases, indicating much less input from young carbon, whereas $\delta^{13}C$ values remain enriched (Fig. 4A,D). This observation opposes the conventional view of increasing $\delta^{13}C$ values with increasing age, because the greatest rate of $^{13}C$-enrichment occurs in the uppermost 30 cm, whereas the large increase in $^{14}C$ (below 50 cm) is not followed by a similar increase in $\delta^{13}C$ (Fig. 4A,D). $\delta^{15}N$ values show a similar increase but only to a depth of 35 cm (Fig. 4B). The relatively high $\delta^{15}N$ values and the increase in the uppermost 30 cm are typical for SOM in subtropical to tropical ecosystems where N is not a limiting nutrient (Martinelli et al., 1999). In fact, soils from temperate forests usually show average $\delta^{15}N$ values of 2.5 $\%_e$, whereas soils from tropical or subtropical forests have reported values of on average 9.1 $\%_e$ (Martinelli et al., 1999). Below 35 cm however, BE shows rapidly decreasing values. Thus, $\delta^{13}C$ and $\delta^{15}N$ values of the BE Oxisol conform only tentatively to the paradigm of increasing values with age and soil depth. In the following, we compare the mechanisms suggested for fractionation processes in the Vertisols with the data from the Oxisol.

4.2.1. C4 input

It is possible that SOM of the BE Oxisol contains a small amount of C4 grasses as the vegetation consists of open woodland. Since no significant land use changes have occurred in this area, the vegetation makeup is considered to have remained relatively stable since European settlement. However, the unconfirmed possibility remains that the $\delta^{13}C$ increase with depth could be due to a greater proportion of C4 grasses hundreds of years ago.

4.2.2. Low pH and decreasing $\delta^{13}C$ and $\delta^{15}N$ values

The drop in pH $\leq 5$ at 35 cm does not coincide with a decrease in $\delta^{13}C$ but corresponds with a sudden decrease in $\delta^{15}N$ along with an increase in inorganic (predominantly NH$_4^+$) N (Fig. 4B). Thus, it appears that the low pH-related fractionation processes discussed for the Vertisols can be applied to this Oxisol: pH above 5 allows for microbial decomposition and nitrification and results in enriched $^{15}N$ values of both the inorganic and organic pool. pH below 5 may result in hydrolytic removal of $^{15}N$-enriched proteins as well as a lack of nitrification. Because the low $\delta^{15}N$ values are associated with an increase in the proportion of the inorganic N pool, accumulation of $^{15}N$-depleted NH$_4^+$ in the clay rich horizon is the most likely explanation for the decreasing isotopic trend.

4.2.3. Selective preservation of C fractions

$^{13}C$-NMR spectra show a strong dominance of O-alkyl carbon and although its relative proportion decreases with depth, it remains the dominant carbon fraction throughout the profile (Table 2, Fig. 5C). As pointed out earlier, O-alkyl C, such as cellulose, is on average 1 $\%_e$ $^{13}C$-enriched compared to bulk plant material (Fig. 8). This relative $^{13}C$-enrichment is not sufficient to explain the increasing $\delta^{13}C$ trend with depth, as the relative proportion of O-alkyl material is highest in the top 10 cm and decreases at 90 cm (Table 2). This implies that the isotopic signature of carbon fractions (e.g. O-alkyl) must have undergone
fractionation to account for the increase in $^{13}\text{C}$. Several studies document that individual biochemical fractions of microbial biomass are significantly $^{13}\text{C}$-enriched in SOM, due to preferred consumption of $^{13}\text{C}$-enriched plant polysaccharides (Macko and Estep, 1984; Huang et al., 1996; Lichtfouse et al., 1995a,b, 1998). If microbial decomposition was more pronounced in this well-drained Oxisol than in the poorly drained Vertisols, significant isotopic fractionations are to be expected in most of the biochemical fractions. Particularly if a significant fraction of the $O$-alkyl material is microbial-derived, a greater $^{13}\text{C}$-enrichment of this fraction than already imparted by its chemistry, is to be expected (Fig. 8).

A different mechanism of selective preservation that might be operating in the Oxisol is physical protection of C through microaggregation. Support for this hypothesis comes from $^{13}\text{C}$-NMR spectra and C/N$_{\text{org}}$ ratios. The unusual persistence of labile $O$-alkyl carbon even at depths may be due to physical protection of this material by formation of microaggregates (Baldock and Skjemstad, 2000). Microaggregation is particularly prominent in Fe-, Al- and Mn-rich soils and Baldock et al. (1992) demonstrated by $^{13}\text{C}$-NMR studies that Al-complexation aids in the protection of labile ($O$-alkyl) material. In addition, the increasing C/N$_{\text{org}}$ ratios below 15 cm suggest that SOM has undergone little decompositional changes and may still comprise relatively labile components (Fig. 4C). Thus, the stability of SOM in Oxisols is suggested to be partly dependent on the formation of organo-mineral associations, namely with Fe and Al.

5. Conclusions

Geochemical and mineralogical data from this study show that isotopic fractionation dynamics in soils are in most cases complex and are affected by a combination of factors. Most importantly, the data indicate that previously assumed responsible factors for isotopic changes, such as the Suess effect, bacterial fractionation, and soil age need to be re-evaluated with respect to questions of quantification and modelling.

Fractionation of SOM by heterotrophic soil organisms has often been used to explain the isotopic enrichment with depth. While the Oxisol shows enrichment with depth, the Vertisols show decreasing isotopic values, despite increasing degree of decomposition. Thus, if $^{13}\text{C}$-enrichment due to microbial biomass occurs in some but not all soil types, the process in itself is either a function of environmental soil conditions or may be masked by more dominant isotopic processes. Consequently, the reliability of curve-fitting functions to assess decompositional fractionation in soils as employed by the CENTURY model or as used by Feng et al. (1999) should be carefully re-examined.

Mean residence time (MRT) of SOM and increasing $\delta^{13}\text{C}$ values were thought to correlate with each other and that with increasing age, degree of fractionation and degree of decomposition increases (e.g. O’Brien and Stout, 1978; Ladyman and Harkness, 1980; Becker-Heidmann and Scharpenseel, 1986; Balesdent and Mariotti, 1996; Bernoux et al., 1998; Bol et al., 1999). In comparison, the $\delta^{13}\text{C}$ and $^{14}\text{C}$ data from the Vertisols and Oxisol do not show the expected relationship between radiogenic and stable carbon isotopes, even if the uppermost intervals in PG and CHI where vegetation change occurred are omitted. The rate of change in MRT with depth is greater for PG than for CHI but both have a much greater MRT than the Oxisol. Thus, this study demonstrates the complexity of $\delta^{13}\text{C}$, $\delta^{15}\text{N}$,
and ¹⁴C dynamics in different soil types and illustrates how vegetation, soil chemistry, soil mineralogy, clay content and pH can effect isotopic trends.

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