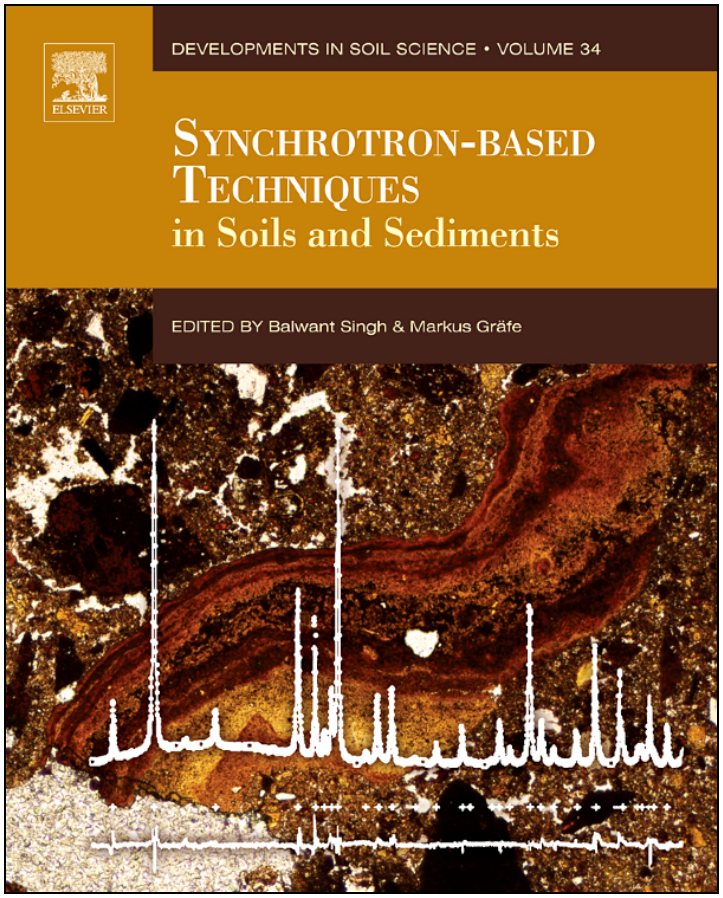

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CHAPTER

10

Organic Carbon Chemistry in Soils Observed by Synchrotron-Based Spectroscopy

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OUTLINE

1. INTRODUCTION

Soil contains the largest pool of terrestrial organic carbon (C) (1500 Pg C) in the biosphere, storing more C than is contained in the biotic (560 Pg C) and atmospheric (760 Pg C) pools combined (Batjes, 1996; Schlesinger, 1997). Organic matter in soil influences soil structure and hence soil water availability, porosity and penetrability, nutrient retention, microenvironment and energy, as well as nutrient resources for microbial and faunal populations, nutrient availability for plant growth, and other properties. On the level of ecosystem services, soil

organic C is critical in balancing atmospheric CO_2 contents with all known ramifications for global climate (Stevenson and Cole, 1999). Therefore, knowledge about the chemistry of organic C is central to understanding soil environments. Notwithstanding this paramount importance of soil organic matter (SOM), insufficient information is available about its chemistry.

SOM has been described as a ubiquitous, heterogeneous mixture composed of naturally occurring organic molecules representing both compounds released from living plant and microbial cells (e.g., extracellular enzymes, surface-active proteins, chelating compounds, etc.) to plant, animal, and microbial residues ranging in size and complexity from simple monomers or organic acids to mixtures of biopolymers (Kelleher and Simpson, 2006; Mahieu et al., 1999; Piccolo, 2001; Solomon et al., 2007a; Sutton and Sposito, 2005). Traditionally, one of the most important processes in the C cycle is seen in decomposition and subsequent humification, whereby various organic molecules found in decaying plant and animal remains are transformed into a more humified material resulting in significant changes in the structural composition of SOM (Wershaw, 1994). This view has recently been challenged by investigations showing both the high chemical complexity stemming from a mixture of simple molecules (Kelleher and Simpson, 2006) and the high spatial complexity at a very fine scale (Lehmann et al., 2008).

Such variations along the decomposition and size continuum, as well as the chemical and spatial complexity of soil organic C, create significant analytical problems and partly explain the current deficiency in our understanding of its chemistry and dynamics, making studies on SOM composition and its implications for the global biogeochemical cycling of C very challenging (Gleixner et al., 2002; Kögel-Knabner, 2000; Solomon et al., 2007a). These challenges have led to recent developments in the analytical techniques that advanced our understanding of the processes underlying its transformations, forcing us to re-examine some of the long-held theories about SOM (Hatcher et al., 2001). Kögel-Knabner (2000, 2002), and Solomon et al. (2007a) emphasized that SOM characterization could further benefit from the progress made in nondestructive micro- and nanoscale X-ray spectromicroscopy techniques to gain new insights about the reactivity, composition, microheterogeneity, physical location of organic materials, and their interaction with soil minerals. In this regard, synchrotron radiation has opened new opportunities for the study of C in soils because the high energy provided significantly improves the spectral as well as the spatial resolution. Recent investigations using synchrotron-based scanning transmission X-ray microscopy (STXM), C (1s) near-edge X-ray absorption fine structure (NEXAFS), and Fourier transform infrared (FTIR) spectroscopy have indicated that these techniques are powerful and noninvasive, and can be used to identify and fingerprint the complex structural characteristics of SOC and dissolved organic C (DOC), as well as to investigate the impact of management on the composition and biogeochemical cycling of organic C at the molecular level in terrestrial ecosystems (Jokic et al., 2003; Kinyangi et al., 2006; Lehmann et al., 2005, 2007; Myneni et al., 1999; Schäfer et al., 2003; Scheinost et al., 2001; Solomon et al., 2005, 2007a,b; Schumacher et al., 2005, 2006).

Soils typically have low amounts of C as compared to pure biological organic matter, which is a challenge for obtaining good spectral data from spectroscopy techniques. If higher energy is provided, it substantially improves the detection limits and yields data that allow better quantification of C chemistry. In addition, the ability to focus the measurement beam close to the physical limits of wavelengths, while maintaining adequate signal strength, is unsurpassed. This feature affords the

possibility to reach very high spatial resolution, which is a key element to the investigation of soil processes (Young and Crawford, 2004). This contribution gives examples for the application of synchrotron radiation for the study of organic C structural chemistry in soils and discusses some recent advances including suggestions for further research. For in-depth methodological discussion of NEXAFS spectroscopy applications to soils and sediments, the reader is referred to Lehmann et al. (2009).

2. SYNCHROTRON-BASED TECHNIQUES AND INSTRUMENTATION RELEVANT TO C CHEMISTRY IN SOILS

This chapter provides examples of two important techniques (synchrotron (Sr)-FTIR and NEXAFS) that can be used in conjunction with synchrotron radiation for the study of C chemistry in soils. Both techniques can be used for analyzing bulk properties and for analyzing spatial distribution of C forms. If spatial resolution is of interest, a microscope is required to scan entire regions of a given sample.

2.1. Synchrotron-Based FTIR Spectromicroscopy

Conventional or globar-sourced FTIR spectroscopy is perhaps the most powerful tool for identifying types of chemical bonds or functional groups in a molecule by producing an infrared absorption spectrum that resembles a molecular "fingerprint." When FTIR spectroscopy is combined with a microscope, the technique is called "FTIR spectromicroscopy." This technique enables probing and identifying the chemical makeup or molecular constituents of biological or complex heterogeneous soil or geological samples from their spatially resolved vibrational spectra on a microscopic scale (Johnston and Aochi, 1996; Lehmann et al., 2007; Marinkovic et al., 2002). Conventional benchtop infrared spectrometers are commonly equipped with thermal (globar) sources that provide infrared light that is comparable to the infrared radiation emitted from a synchrotron (Miller and Dumas, 2006; Miller and Smith, 2005). Yet, if the aperture for spatial investigations is decreased to limit the field of view to a small region of interest, the brightness of conventional benchtop infrared sources is by two to three orders of magnitude too low compared to synchrotron radiation (Bonetta et al., 2002; Raab and Martin, 2001), thus resulting in diffraction effects. It is possible to circumvent the shortcomings of this conventional technique by replacing the light source of a conventional FTIR spectromicroscope with synchrotron radiation, that is, electromagnetic light emitted by charged particles (electrons, photons, ions) that are moving at relativistic speed of light following a curved trajectory in particle accelerators called synchrotrons, typically called synchrotron radiation-based FTIR (Sr-FTIR) microspectroscopy.

The primary advantage of synchrotron infrared radiation is its brightness (defined as the photon flux or power emitted per source area and solid angle), which is 100-1000 times greater from a synchrotron source than from a conventional source (Carr et al., 1995; Miller and Dumas, 2006) and results in better spectral properties and better signal-to-noise ratios (Fig. 10.1A). This brightness advantage does not arise because the synchrotron produces more energy, but because the effective source size is small and the light is nondivergent and emitted into a narrow range of angles leading to more light being available on smaller spot sizes (Carr, 1999, 2001; Miller and Dumas, 2006; Miller and Smith, 2005; Raab and Martin, 2001; Wetzel et al., 1998). The high brightness of synchrotron sources therefore allows smaller regions to be probed in shorter lengths of time by maintaining acceptable signal-to-noise ratios. This is shown in Fig. 10.1 for a spot size

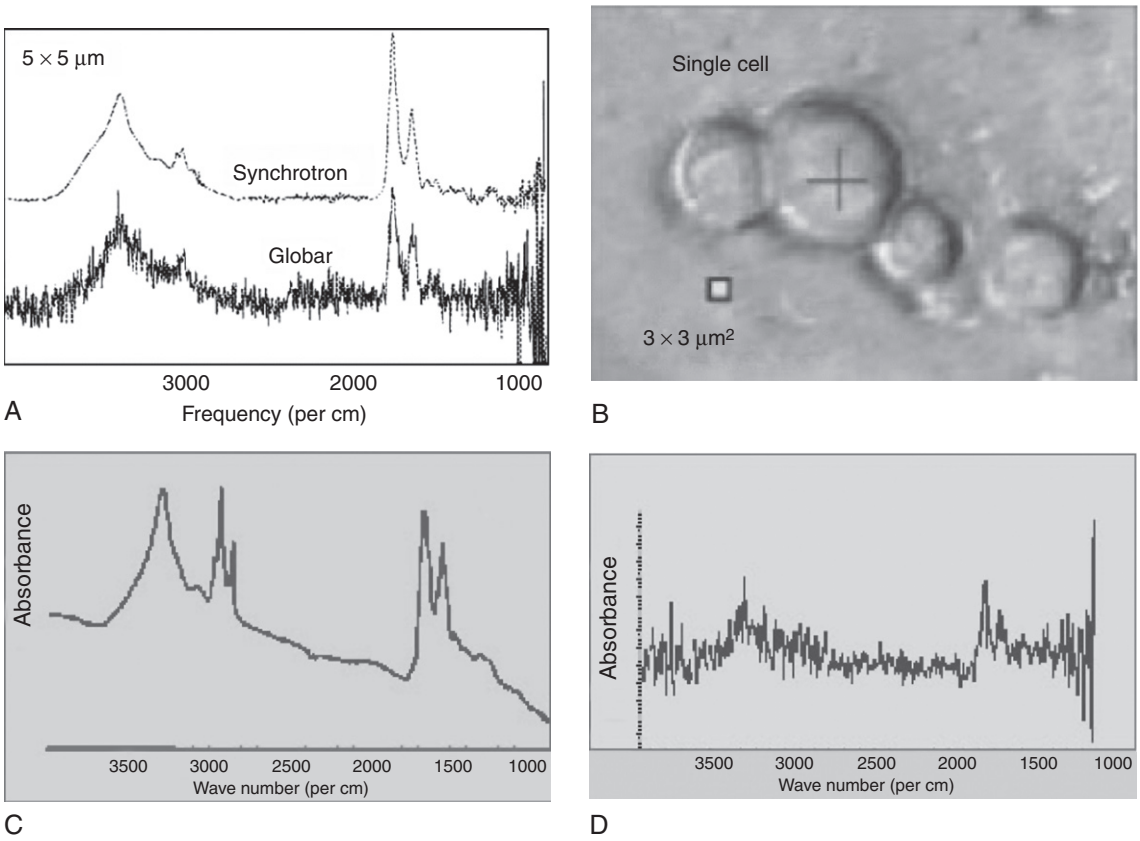

FIGURE 10.1 Comparison of SR-FTIR and conventional FTIR microspectroscopy. (A) Infrared spectra of a single red blood cell collected with a synchrotron versus globar source. With synchrotron light, a very good signal to noise ratio of a very small area (5 × 5 µm aperture size) with high ultra-spatial resolution is obtained (top) in contrast to a globar source, where a poor spectrum with low signal-to-noise ratio is obtained (bottom) illustrating how the brightness advantage of the synchrotron leads to dramatically improved signal to noise ratios (from Miller and Dumas, 2006). (B) Visible image. (C) and (D), Comparison of synchrotron and globar-sourced FTIR microspectroscopy shows a faster data collection with synchrotron light. With synchrotron light (C), only 16 s and 32 scans are needed to obtain a high-quality spectrum of a small area (3 × 3 µm aperture size); with a conventional globar source (D), at a larger area of 6 × 6 µm, even when using 1000 scans and 500 s only a very poor-quality spectrum can be obtained. (from Dumas, 2003; Yu, 2004; with permission from the publisher).

of 3 by 3 µm for Sr-FTIR with a short acquisition time compared to 6 by 6 µm for a globar source with a long acquisition time. The technique is a rapid, direct, and nondestructive analytical approach, capable of exploring the molecular chemistry within microstructures of biological and environmental samples with a high signal-to-noise ratio at fine spatial resolution (Bonetta et al., 2002; Lehmann et al., 2005; Marinkovic et al., 2002; Miller and Dumas, 2006; Raab and Martin, 2001; Vogel et al., 2002; Wetzel, 2001; Wetzel et al., 1998; Yu, 2004; Yu et al., 2003). Sr-FTIR spectroscopy is able to provide information related to the quantity, composition, structure, and distribution of chemical constituents and functional groups in humic

fractions (Solomon et al., 2005, 2007a), stable soil aggregates, and black C particles (Lehmann et al., 2005, 2007) and can capture a wider spectral range than conventional FTIR can, and therefore allows more detailed structural information to be extracted. This analytical approach can be used to increase the understanding of the spatial (microscale) distribution of soil organic C at the molecular level and improve understanding of organomineral interactions and C sequestration in soils (Lehmann et al., 2007) that would not be possible without the use synchrotron radiation.

However, investigation of the structural composition of organic C in soils using FTIR spectromicroscopy and subsequent qualitative and quantitative interpretation of the spectra to describe the changes in organic matter chemistry is at times difficult due to the influence of O–H stretching and bending of sorbed water, clay minerals, and metal oxides, Si–O–Si stretching, carbonates, and other inorganic soil constituents that lead to overlap between individual absorption bands of organic and inorganic soil components (Table 10.1) and the preponderance of poorly defined baselines (Hempfling et al., 1987; Rumpel et al., 2001). These need to be considered to avoid incorrect attribution and allow relative quantification.

This problem is especially important in the complex lower region of the spectrum (between 1450 and 600 cm^{-1}), which is usually known as the "fingerprint region," as chemical bonds from various sources in different environments will absorb varying intensities and at varying wave numbers. A typical FTIR spectrum can be divided into two regions, where the region above 1450 cm^{-1} contains relatively few, and less complex, diagnostic peaks (Table 10.1). In contrast, the complexity in the FTIR spectra below 1450 cm^{-1} normally exhibits several overlapping bands of unknown quantity and source in a heterogeneous matrix such as mineral soil, that create difficulties in assigning the absorption bands to a specific bond and correlating these bonds to organic C functionality. For example, the strong band between 1150 and 1000 cm^{-1} of FTIR spectra taken from soils is usually attributed to the C–OH stretching of polysaccharides. However, this band overlaps with the Si–O–Si stretching of silicate bands (1200-970 cm^{-1}) in soil, and may undermine the identification of the polysaccharide peak position, as well as the quantification of this functional group from the peak intensity. Thus, the result may not necessarily relate to or reflect the amount of this functional group present in the sample. Although the FTIR peaks of soils and organic matter are often too complex to provide simple visual qualitative and quantitative data (Janik et al., 1995), some of these problems can be overcome by using the unique spectral features that can be obtained from FTIR spectral libraries of pure reference compounds followed by cluster analysis (Dziuba et al., 2007) or by spectral subtraction of digital FTIR spectra of the interfering pure mineral or inorganic soil constituent (Painter et al., 1981; Rumpel et al., 2001; Skjemstad et al., 1993). Chemometrical methods such as multivariate data analysis have also been used in the past in order to interpret the wealth of information generated by FTIR spectroscopy or to quantify the content of specific compound classes, for example, fat, protein, polysaccharides, and microbes (Gordon et al., 1993; Luinge et al., 1993). Multivariate data analysis is often associated with regression modeling, that is, to model the relationships between two sets of measurements (Rumpel et al., 2001). Any data matrix can be represented as just a few bilinear projections, principal components, or partial least squares in latent variables (Wold, 1989). The use of partial least squares focuses on predictive modeling and the technique was successfully applied in soil science to predict soil properties from their midinfrared spectra (Janik and Skjemstad, 1995; Janik et al., 1995). Nonetheless, quantification of FTIR spectra remains a challenge and requires careful consideration of its limitations.

TABLE 10.1 Functional group frequencies of the main FTIR bands of common soil components

Soil components	Peak positions[a] Wavenumber (cm^{-1})
Organic components	
O–H stretching of carboxylic acids, phenols, alcohols	3500-3200
N–H stretching of amines, amides	3400-3200
C–H stretching of CH_2; CH_3 attached to aromatic units	3150-2920
Asymmetric aliphatic C–H stretching of CH_3 and CH_2	2970-2870
Symmetric aliphatic C–H stretching of CH_3 and CH_2	2870-2820
C=O stretching of carboxylic, quinones, amides, ketones, esters, aldehydes	1750-1630
Aromatic C=C vibrations and C=C stretch of aromatic C in lignin	1650-1530
Amide N–C stretch, side chain vibration of -NH and CH_2 stretch vibrations of amino acid side chains	1530-1510
C–H bending of $–CH_2–$ and CH_3	1465-1384
C–O stretching, O–H bending of COOH	1260-1200
C–OH stretching of polysaccharides	1170-950
Inorganic components	
Clay minerals and oxides	
O–H stretching of structural OH	3750-3300
O–H bending of structural OH	950-820
Si–O–Si stretching	1200-970
O–Si–O deformation or bending	550-400
Al–OH stretching	950-900
Mn–O stretching	675-570
Fe–O stretching	575-400
Sorbed water	
O–H stretching	3600-3300
O–H bending	1650-1620
Carbonates	1600-1300
	1300-850
	900-670
Phosphates	1200-1100
	600-500
Sulfates	680-600

[a]Peak assignments for organic and inorganic soil constituents were modified from Farmer (1964), Wieckowski and Wiewiora (1976), Stevenson (1994), Gressel et al. (1995), Janik and Skjemstad (1995), Jackson and Mantsch (1996), Johnston and Aochi (1996), Haberhauer et al. (1998), Rodriguez et al. (1998), Almendros et al. (2003), Guan et al. (2005), Lehmann et al., (2005, 2007), Solomon et al. (2005, 2007a).

2.2. Synchrotron-Based NEXAFS Spectroscopy

NEXAFS spectroscopy is a powerful spectroscopic method enabled by advances in X-ray microfocusing techniques and access to a high-flux source of X-ray photons from synchrotron light sources. The word NEXAFS is used in this publication synonymous to XANES. NEXAFS is typically used for so-called soft X-ray spectroscopy with a photon energy less than 2000 eV as with C, whereas the term XANES is applied for tender (2000-3000 eV) and for hard (>3000 eV) X-ray spectroscopy. Carbon NEXAFS features arise when incident photon energy from synchrotron radiation is increased throughout the absorption *K*-edge (Stöhr, 1992), which is at a specific energy level for each element (284 eV for C), beyond the ionization threshold (290 eV for C). At this energy level, core electrons (in the K shell) are promoted to higher orbitals (above the *K*-edge) or completely removed (above the ionization threshold) by the photons (Ade et al., 1992; Brandes et al., 2004; Jacobsen et al., 2000; Stöhr, 1992). Using a tunable monochromator, C NEXAFS spectra close to the *K*-edge can be collected either by measuring the absorption of the photons, in fluorescent mode, where the emitted photons are monitored, or by determining total electron yield, in which the neutralization current from the sample is recorded (Gutiérrez-Sosa et al., 1999; Jokic et al., 2003; Rothe et al., 2000; Stöhr, 1992). The edge region usually shows the largest variation in the X-ray absorption coefficient, and is often dominated by intense narrow resonances (Stöhr, 1992). The excited phase of the inner-core (1s) electron is characteristic of the structure of the C functional group chemistry, and can be correlated to specific C forms. This is subject to the caveat that C in different electronic environments may have vastly different absorption coefficients, and in many cases absorption bands from different organic functional groups may overlap (Ade et al., 1992; Brandes et al., 2004; Stöhr, 1992).

NEXAFS is highly element-specific because the X-ray absorption edges of different elements have different energies (Stöhr, 1992). Therefore, water does not interfere with the measurement of C, nor does any other element such as iron (Fe), which is a major drawback for analyzing C forms in soil by nuclear magnetic resonance (NMR) spectroscopy. Developments in the quantification of functional group chemistry of NEXAFS spectra are still required however, and general agreements about normalization and peak attributions are still pending (Lehmann et al., 2009).

When NEXAFS is coupled to STXM, spatially explicit information can be obtained with currently up to 30-50 nm spatial resolution. This technique is then typically called NEXAFS spectromicroscopy (the term "microspectroscopy" is sometimes used to indicate the ability to measure very small spot sizes, but without the ability to map entire areas). NEXAFS spectromicroscopy in conjunction with STXM requires the beam to penetrate the sample and absorption of the transmitted signal is recorded. Such transmission experiments demand sufficiently thin samples, but have the advantage that interferences from sample carrier material or other contamination can be completely removed mathematically. Sample preparation for soil analyses depend on the objectives of the experiment and bear certain constraints and challenges that are discussed in detail elsewhere (Lehmann et al., 2009). For example, an assessment of C forms within microaggregates will require sectioning to obtain sufficiently thin sample material. If C on surfaces of aggregates or fine clay particles are of interest, an analysis of entire assemblages may suffice and afford the possibility to measure a larger number of samples.

The enhanced chemical sensitivity of C (1s) NEXAFS spectroscopy and the high spatial resolution of X-ray microscopy now afford the opportunity to adapt these conjugated novel spectromicroscopy techniques to investigate the nanoscale processes in the C chemistry and

structural assembly of soil aggregates at a much higher spatial resolution (30-50 nm) than ever before. Additionally, other advanced *ex situ* invasive spectroscopy techniques such as X-ray photoelectron spectroscopy, auger electron spectroscopy, and secondary ion mass spectrometry, which must often be performed under adverse experimental conditions, for example, sample drying, ultrahigh vacuum, heating, or particle bombardment, may alter the nature of samples, yielding misleading data as a result of experimental artifacts (Sparks, 2003). In contrast, these *in situ* X-ray spectromicroscopy techniques provide a detailed understanding of submicroscopic architectural arrangement of organic C functionalities, other spatial features, and element-specific information about the interactions that have practical relevance to the stabilization of organic C in soils while maintaining the spatial integrity of the sample. The latter is a methodological issue that has to be carefully verified (Lehmann et al., 2009).

Combining the potentials of these nondestructive high-resolution micro- (Sr-FTIR) and nanoscale (STXM-NEXAFS) spectromicroscopic approaches yields element-specific biogeochemical evidence about the *in situ* spatial arrangement of organic C functionalities, minerals, metal ions, and other architectural features of organomineral assemblages. Such an approach will help bridge the gap between the dynamic multiscale interactions and processes involved in the stabilization of organic C in the soil system.

3. RESOLVING KEY QUESTIONS IN SOIL BIOGEOCHEMISTRY

The following sections provide a survey of different questions to which the two methods discussed in this chapter have proven to contribute unique insight. This overview is not intended to give a comprehensive review of synchrotron-based NEXAFS and FTIR studies in general, but highlight recent advances made in applications to soil organic C research and those studies outside soils that are of relevance to future soils research.

3.1. Functional Group Chemistry of C

3.1.1. *Synchrotron-Based FTIR Spectroscopy*

Sr-FTIR (4000-400 cm^{-1}) measures the contribution from vibrations of particular organic and inorganic functional groups within molecules (Bonetta et al., 2002; Marinkovic et al., 2002). Sr-FTIR spectra contain a variety of bands that are diagnostic. These diagnostic properties include the appearance or loss of vibrational bands, changes in relative band intensities, shifts in band frequency, or change in the lineshape of a particular band (Johnston and Aochi, 1996), which can serve as a valuable tool not only to characterize the principal classes of chemical groups of which SOM is comprised but also to investigate management-induced molecular-level changes in the composition of SOM (Solomon et al., 2005, 2007a). Equally important to the role Sr-FTIR spectroscopy has played in the identification and characterization of soil components, is its contribution to our understanding of molecular-level chemical processes involving solid-solution, solid-vapor interfaces (Johnston and Aochi, 1996), and microscale surficial and spatial associations in organomineral assemblages and other solid soil components such as black C particles (Lehmann et al., 2005, 2007).

Infrared microspectroscopy has been used to examine numerous plant and animal tissues, even before combining the infrared microscope and synchrotron sources (Miller and Dumas, 2006; Wetzel and LeVine, 1999). The assignments of various spectral features and their relationship with the molecular composition of the source material in biological samples have been the subject of numerous publications, which have been reviewed recently by

Jackson and Mantsch (2000). At times, ambiguity in distinguishing between, for example, aromatic and carboxylic C functionalities of organic C in the region between 1800 and 1500 cm^{-1}, especially in black C-rich soils, makes this method a less suitable technique to assess the molecular-level composition and oxidation of black C on surfaces and across sections of particles in complex natural systems (Lehmann et al., 2005). However, armed with information about the climate, vegetation, parent material, soil type, and detailed spectral features from spectral libraries of ecologically relevant organic compounds such as proteins, lipids, nucleic acids, and carbohydrates (Fig. 10.2), a much better assessment or prediction of the contribution from vibrations of various SOM sources and components to the bulk SOM or dissolved organic matter (DOM), can be made. Such practices are widely employed in biomedical research to obtain important details about variations in nucleic acid, protein, and lipid content or structure (Miller and Dumas, 2006). In combination with its high spatial resolution, Sr-FTIR spectromicroscopy can probe the molecular-scale structural composition of C in individual cells of tissues at subcellular resolution (Miller and Dumas, 2006), thus opening new research avenues in soil biology.

3.1.2. *Near-Edge X-Ray Absorption Fine Structure Spectroscopy*

Synchrotron storage rings permit NEXAFS studies at very low levels of organic C, such as in films of humic fractions extracted from highly complex matrices as found in soil (Schäfer et al., 2003, 2005; Solomon et al., 2005, 2007a,b) and in environmentally relevant model systems of pure standards designed to serve as simplified analogs of SOM components (Boese, 1996; Boese et al., 1997; Kaznacheyev et al., 2002; Zubavichus et al., 2005; Solomon et al., 2009). For example, C (1s) NEXAFS has been effectively used in the past to study the structural composition of coal (Cody et al., 1995, 1996), humic substances (Rothe et al., 2000; Scheinost et al., 2001; Schmidt et al., 2000; Solomon et al., 2005, 2007a), soil colloids (Schäfer et al., 2003; Schmidt et al., 2003; Schumacher et al., 2005), DOM in soil (Schumacher et al., 2006), total soil (Jokic et al.,

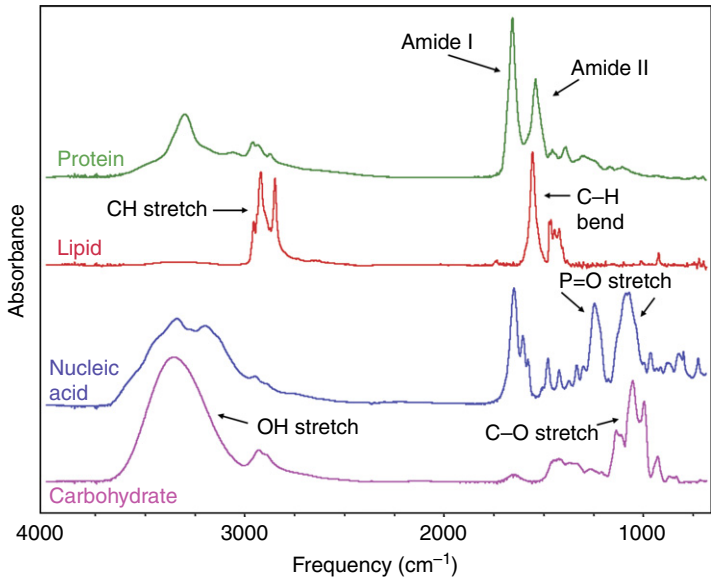

FIGURE 10.2 FTIR spectra of biological components highlighting the most prominent absorption features of biologically relevant pure organic compounds. Spectra for a protein (myoglobin), lipid (dimyristoylphosphatidylcholine, DMPC), nucleic acid (poly-A), and carbohydrate (sucrose) are shown. (adapted from Miller and Dumas, 2006; with permission from the publisher).

2003; Lehmann et al., 2008), and biopolymers such as amino acids and peptides (Boese, 1996; Boese et al., 1997; Kaznacheyev et al., 2002; Stewart-Ornstein et al., 2007; Zubavichus et al., 2005), which have led to unique and novel insights about the structural composition of organic moieties, chemical processes occurring in soils, and how these change as a result of land-cover changes.

Carbon *K*-edge investigations of the molecular-level organic C speciation of thin films of humic fractions usually reveal spectra with multiple energy positions of the main 1s-π* transitions in the fine structure region (284-290 eV) (Fig. 10.3; a complete list of peak positions is shown in Lehmann et al., 2009). Two ionization thresholds (IPs) were set as described in Schäfer et al. (2003, 2005) and Solomon et al. (2005) for C(1s) spectrum deconvolution by setting two arctangent functions at 290.5 eV for aromatic/aliphatic carbon (Hitchcock and Ishii, 1987; Hitchcock et al., 1992) and at 292.0 eV for hydroxylated aromatic C with full width at half maximum (FWHM) of 0.4 eV to generate a continuum of spectrum up to 294.0 eV. The IPs magnitude was assessed by the atomic ratio of C to O tabulated in Artinger et al. (2000). The FWHM of the Gaussian peaks (G) was set at 0.4 eV and six Gaussian functions (G1-G6) representing the main 1s-π* transitions near 284.4 (G1), 285.2 (G2), 286.7 (G3), 287.3 (G4), 288.6 (G5), and 289.3 (G6) eV were resolved (Cody et al., 1998; Schäfer et al., 2003). Additionally, two σ* transitions at 290.2 eV (σ^1) and 291.5 eV (σ^2) were simulated using simplified Gaussian shape function by Solomon et al. (2007a). However, since fine structures in the C NEXAFS region above 290 eV tend to be very broad and overlap with each other (Cody et al., 1998; Schäfer et al., 2003), only the main 1s-π* transitions were used for both qualitative and semiquantitative molecular-level interpretation of the NEXAFS results as done in most studies of a heterogeneous matrix such as soil (Schäfer et al., 2003, 2005). The C 1s-π* transition near 284.4 eV is associated with quinone type-C, such as benzoquinone and with protonated and alkylated aromatic-C or heteroatom-substituted aromatics (Schäfer et al., 2003, 2005; Solomon et al., 2005). The resonance near 285.2 eV is assigned to aromatic C (protonated and alkylated to carbonyl-substituted aromatic C) and possibly olefinic C (Ade and

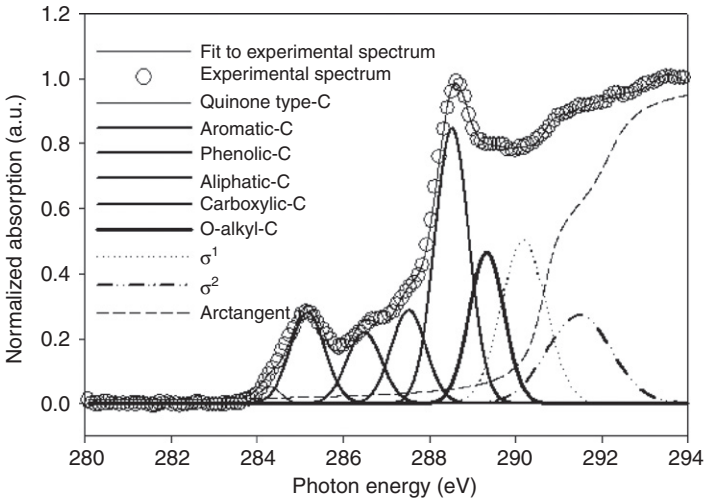

FIGURE 10.3 Speciation of soil organic C using deconvolution of C (1s) near-edge X-ray absorption fine structure spectra showing the main 1s-π* and 1s-3π/σ* transitions, and two σ* transitions and arctangent step functions in humic fraction extracted from soil (details of peak assignments are discussed in the text; adapted from Solomon et al., 2007a; with permission from the publisher).

Urquhart, 2002; Cody et al., 1998; Lehmann et al., 2005). The absorption band near 286.7 eV likely corresponds primarily to phenolic C including O-substituted aryl C indicative of lignin and possibly to ketonic C and phenyl C attached to amide groups (Ade and Urquhart, 2002; Cody et al., 1998; Rothe et al., 2000; Schäfer et al., 2003). The 1s-3p/σ* transitions near 287.3 eV are mainly due to aliphatic C of CH_3, CH_2, and CH nature, while the strong resonance near 288.6 eV represents C 1s-σ* transitions of carboxylic C (Cody et al., 1998), but may also include amide C at a slightly lower energy of 288.2 eV (Lawrence et al., 2003).

Based on available data to date, NEXAFS analyses were able to demonstrate the subtle but persistent changes in SOC functional group chemistry of SOM as a result of cultivation (Solomon et al., 2005, 2007a). Such changes in the inherent molecular structures of SOM may exert a considerable influence on biogeochemical cycling of C and bioavailability of essential nutrients present in association with SOM. In contrast, C (1s) NEXAFS of SOM extracts from five very different forest soils in New Zealand, USA, Brazil, Kenya, and Panama, showed almost identical spectral features (Lehmann et al., 2008). Such analyses of total organic matter typically yield peaks near 285, 286.7, and 288.6 eV (Lehmann et al., 2008; Scheinost et al., 2001; Solomon et al., 2005, 2007a) similar to humic substances isolated from groundwater (Schäfer et al., 2003, 2005). In comparison, DOC characterized in pore water of rock formations showed dominance of peak energy at 288.5 eV, which is indicative of carboxylic C forms with only small features slightly around 285.0 eV (Courdouan et al., 2007).

Conjugated synchrotron STXM and C 1s-NEXAFS was also widely used as a direct solid-state technique to resolve nanostructures of polymers (Smith et al., 2001) and to fingerprint C in biological materials (Hitchcock et al., 2005; Lerotic et al., 2004), where radiation exposure is controlled to avoid damage to the susceptible C=O bond (Braun et al., 2005; Rightor et al., 1997). High concentrations of C in uniform polymer-layered samples (Ade and Urquhart, 2002) and black C (Lehmann et al., 2005) permit NEXAFS data filtering, thereby improving the signal-to-noise ratio of the images allowing to effectively fingerprint the various C functionalities present in these samples. Sample preparation and biases have to be carefully considered, especially with respect to radiation damage of labile microbial matter or oxidizable compounds (see discussion in Lehmann et al., 2009).

3.2. Spatial Organization of C Forms in Microstructures

The most compelling strength of synchrotron radiation is that it allows spectroscopy with much greater spatial resolution compared to alternative energy sources. This enables mapping not only of C contents, but also of C forms when coupled with NEXAFS or FTIR. Several studies have shown by now that it is possible to obtain spatially explicit information about C functional group chemistry in soils using NEXAFS (Kinyangi et al., 2006; Lehmann et al., 2005, 2007, 2008; Liang et al., 2006; Wan et al., 2007) or FTIR (Lehmann et al., 2007). Therefore, the existence of small-scale spatial heterogeneity is an important characteristic of soil C (Fig. 10.4). The difference in C forms on a scale of hundreds of nanometers determined by NEXAFS spectromicroscopy was shown to be greater than the difference in C characteristics between forest soils of different ecoregions and climates on a global scale (Lehmann et al., 2008). Organic C in pores shows, for example, very different functional group chemistry than C on mineral surfaces (Kinyangi et al., 2006) and none of the C NEXAFS spectra on the spatial scale resolvable by STXM resembled the C NEXAFS spectra of total organic C in soils from different forest ecosystems, but rather resembled

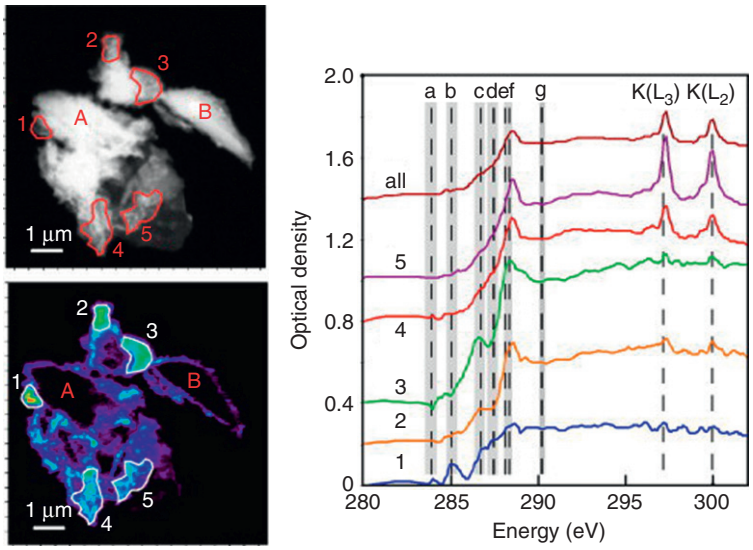

FIGURE 10.4 Carbon *K*-edge NEXAFS analyses using STXM of a Cambisol assemblage. (Wan et al., 2007; with permission from the publisher).

identifiable compounds derived from plants or microorganisms (Lehmann et al., 2008). These observations challenge the notion of soil organic C being mainly composed of chemically complex macromolecules and strongly suggest the need to investigate the specific functional group chemistry of organic C at high spatial resolution.

An important strength of the technology is undoubtedly the high spatial resolution. Obtaining representative samples and being able to measure sufficient sample material is both a methodological and statistical issue that needs to be further developed. For obtaining accurate spatial information on such a fine scale, careful consideration needs to be given to sample preparation, spectral quantification, and possible radiation damage (Lehmann et al., 2009).

3.3. Interactions of C with Soil Matrix

3.3.1. Surface Interactions of Organic C and Minerals

Interactions between soil organic C and mineral surfaces have been investigated since the seminal works by Emerson (1959) and Edwards and Bremner (1967). The nature of the interaction may not depend only on the organic matter forms, but also on the surface chemistry of the minerals (Kleber et al., 2007). Much of the work on interactions has involved experiments using decrease in carboxyl C forms physical fractionation either with or without isotope tracing or adsorption experiments. The strength of these assessments is that the dynamics of mass flow can be quantified; for example, the incorporation of C into a fraction that interacts with mineral surfaces. However, physical fractionation protocols can never completely resolve whether components in the same fraction are also spatially associated in the unfractionated soil or are merely separated by the same fractionation method. While providing valuable information about differential interaction between varying organic molecules and minerals, adsorption experiments only imperfectly simulate *in situ* conditions due to the necessity to disperse the soil in commonly used batch methods.

In contrast, synchrotron-based NEXAFS and FTIR spectromicroscopy techniques are able to provide unequivocal information about spatial association of organic matter and minerals

in situ. Using a combination of NEXAFS with STXM, for example, organic C forms can presently be mapped with a spatial resolution of up to 30 nm. This resolution is sufficient to distinguish between organic matter in micrometer size pore structures and on surfaces of minerals as shown by Kinyangi et al. (2006). Observations across organomineral interfaces may be a step forward in identifying specific bonding mechanisms. In the example shown in Fig. 10.5, spectral properties appear to change with distance from the mineral surface. Peak height near 287.3 eV (most likely aliphatic C in either fatty acids or carbohydrates, but possibly containing some phenolic C) tended to increase with proximity to the mineral surface (Fig. 10.5). This type of information may aid in identifying bonding mechanisms between organic matter and minerals in soils. Challenges are possible spectral distortions with increasing optical density as a result of mineral phases. This could have led to a decrease in carboxyl C forms near the minerals, as shown Fig. 10.5. An interesting observation is the pronounced peak between 285.0 and 285.5 eV, which most likely originates from aromatic C functional groups, near mineral surfaces. Additional thinner sections that allow

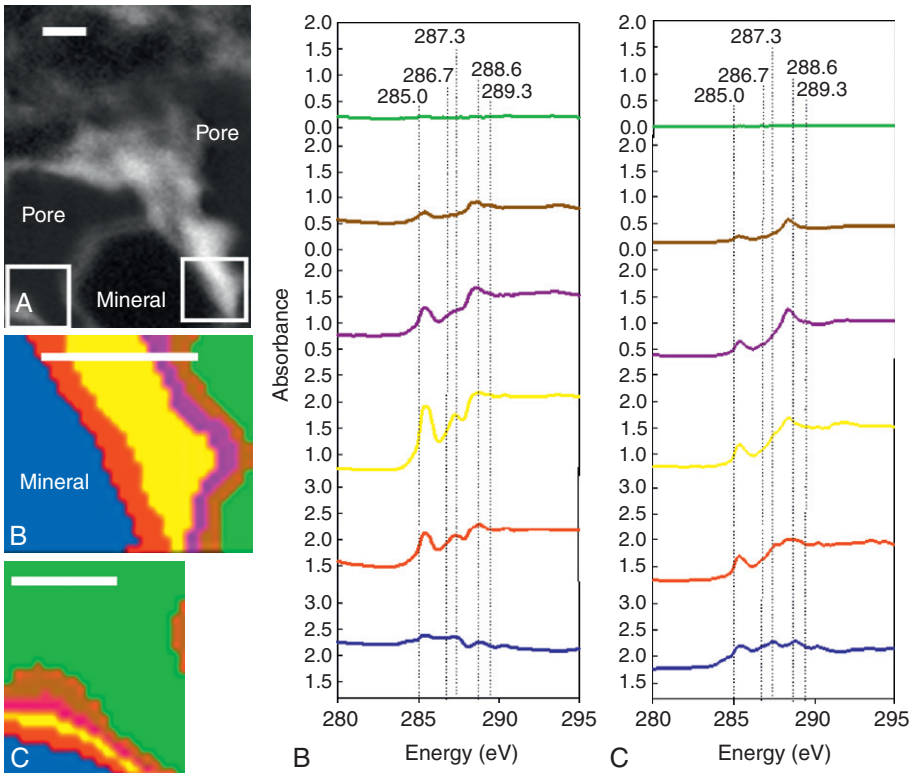

FIGURE 10.5 C(1s) NEXAFS spectroscopy (50 nm resolution) of organic C close to mineral phases of a kaolinitic Oxisol in Kenya (detail of a section shown in Kinyangi et al., 2006). (A) Difference map indicating optical density of total C (by subtracting optical density between 280 and 282 eV from 290 to 292 eV; white areas indicate C and white square shows the area for which cluster analysis was performed); (B), (C), cluster maps of different organic C forms with their corresponding spectra for each cluster color in image. White bars indicate 1 μm.

assessment of organomineral mixtures by excluding ambiguity of spectral distortions as a result of high optical density are needed. Increased abundance of heterocyclic N in organomineral admixtures as compared to coatings and microbial matter (Lehmann and Solomon, 2008) also points at cyclic organic matter playing a role in the formation of organomineral interactions. Some indications also exist from research on lake colloids where organic matter associated with minerals was characterized by greater proportions of aromatic C (Schäfer et al., 2007). This will need to be tested more rigorously in the future for soil organic C interactions with different minerals.

While this view of the spatial association between organic C and minerals is an important step forward, it does not prove interaction. Just for reason of spatial proximity, we cannot conclude on the existence or strength of bonding between organic matter and minerals. Nonetheless, correlation between organic C forms and minerals is able to provide sound evidence for the type of organic matter that is associated with minerals (Lehmann et al., 2007). Using SR-FTIR spectroscopy, Lehmann et al. (2007) correlated different C functional groups not only with minerals, but also with certain O–H groups indicative of kaolinite. The spatial relationship between aliphatic C groups (at 2922 cm^{-1}) and clay O–H (at 3695 cm^{-1}) was strong for an Oxisol rich in highly weathered secondary clay minerals, but very weak for an Alfisol with a predominance of 2:1 clay minerals. An example for the kaolinitic Oxisol is shown in Fig. 10.6 using spatial Sr-FTIR images taken by an MCT-B detector, which expanded the energy range to 400 cm^{-1} wave numbers to capture Al mineral features. This example does not show a significant difference in the relationship between absorbance at 915 cm^{-1} indicative of Al–O (Rodriguez et al., 1998) and 2922 cm^{-1} as compared to kaolinite O–H at 3695 cm^{-1}. This example also shows no spatial similarity of the distribution of aromatic C (at 1589 cm^{-1}) with minerals at the scale investigated here.

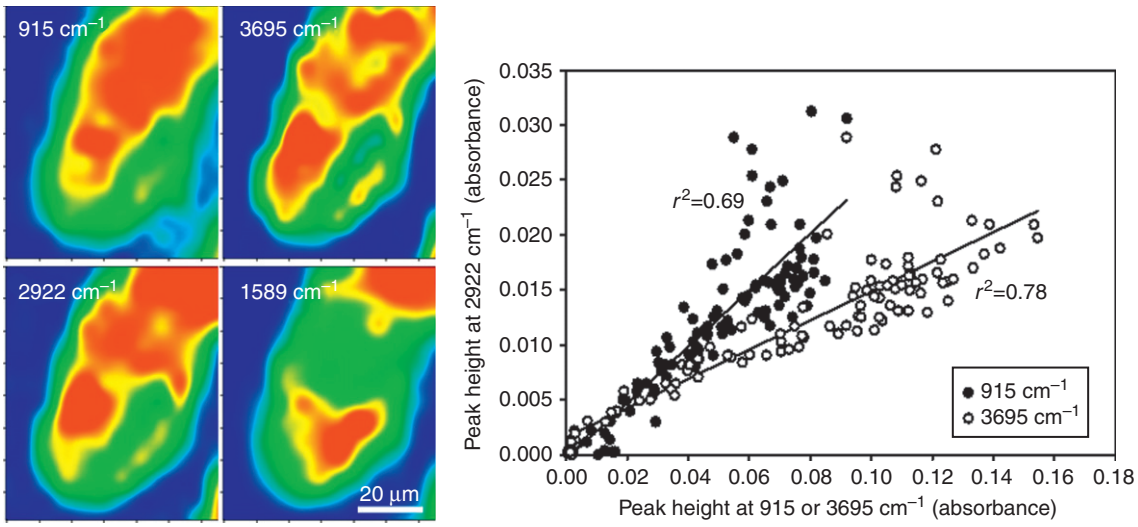

FIGURE 10.6 FTIR analysis of a thin section obtained from a kaolinitic Oxisol (described in Lehmann et al., 2007) using beamline U10B at the National Synchrotron Light Source (aperture 10 µm, step size 6 µm; MCT-B detector). Larger contents at the respective wave number are indicated by red, low contents by blue.

Similar assessments are possible with NEXAFS, but have not yet been reported for soils. Apart from stoichiometric relationships between total elemental contents of Ca, Al, Si, or Fe with C (Wan et al., 2007), the chemical forms of these elements can also be related to organic C forms by using NEXAFS. Spectral properties of Ca compounds are different from each other and ionic free or adsorbed Ca^{2+} can for example be clearly distinguished from biogenic Ca or geogenic Ca (Ko et al., 2007; Obst et al., 2007). Multielement approaches with NEXAFS spectromicroscopy to resolve processes of interactions are very promising.

However, even the spatial resolution of NEXAFS with currently about 30 nm, may prove to be insufficient to identify the functional groups that link organic C with functional groups on mineral surfaces. Sizes of goethite and hematite crystals are typically 13-26 nm and 23-39 nm, respectively (Anand and Gilkes, 1987) and kaolinite crystals in soil may measure 100 nm (Singh and Gilkes, 1992). These crystal sizes require high spatial resolution that is only recently available. Bond lengths of carboxyl C–O or O–H are even smaller, with about 0.1 nm (Leiserowitz, 1976). Therefore, the spatial resolution of current STXM using NEXAFS of about 30 nm is not yet sufficient to identify individual bonding structures at organomineral interfaces. Future developments in improving X-ray focusing will invariably be limited by the wavelength of X-rays near the C *K*-edge, which is circa 4 nm.

Identifying spatial association between organic C and minerals that are below the spatial resolution of STXM may be achieved by relating the optical density below the C *K*-edge to NEXAFS features at the C *K*-edge. This optical density below the C *K*-edge is a relative measure for the mineral content at a certain location. Comparison of regions within a given thin section that shows high mineral admixture to those with low mineral admixture can be instructive in identifying functional group chemistry that is colocated with minerals. Kinyangi et al. (2006) showed, for example, that higher optical densities were associated with carboxyl C, C=N, and C=O forms, whereas lower optical densities were associated with aromatic C=C, C–H, and C=O. Such conclusions require careful consideration of the procedure for sample preparation and the nature of the sample. Even very thin sections of 100-200 nm may contain layers of organic and mineral matter that may not necessarily be in contact with each other, yet are captured in the same analysis that integrates chemical properties for any given point through the absorbed energy. Multiple analyses of different sections should yield reproducible trends that can then be unambiguously interpreted. Also spectra distortions at greater optical densities induced by minerals need to be considered as mentioned above.

Another approach to identifying actual bonding may emerge by looking at changes in spectral signatures as a result of spatial association between organic C and minerals that can be linked to a mechanism of interaction. For example, Edwards and Myneni (2006) observed a peak shift of the $1s \rightarrow \pi^*$ transition of hydroxamate in acetohydroxamic acid from 288.3 to 288.5 eV by protonation in aqueous solution. Nachtegaal (2003) reported a shift of the peak from 288.0 to 288.2 eV in humic acid extracted from a bog in New Hampshire, USA, as a result of a pH increase from 4 to 7. Helpful in this respect is the parallel investigation of N and O NEXAFS together with C (Edwards and Myneni, 2006). Slight changes in peak intensities for peaks in the energy range of 288-289 eV (mostly carboxyl C) were also caused by additions of Ca to a humic acid extract from soil (Christl and Kretzschmar, 2007). Complexation of benzoic acid or extracted humic substance with different metals caused significant changes in peak height near 288.5 eV with a decrease noted for U(IV) in comparison to Na (Plaschke et al., 2005). It is in principle

conceivable to assess the existence of specific binding mechanisms, for example by cation bridging or hydrogen bonding, at the organo-mineral interface by observing changes in peak intensity or peak position. This may only be possible in well-constrained studies where the source materials can be quantified independently, such as in batch experiments, and may differ as a function of the metal. No changes in peak positions or intensity were found as a result of interaction of humic acid extracts with dissolved Al^{3+}, whereas a significant shift of the C 1s(C=O)→$1\pi^*_{C=O}$ transition by 0.7 eV to lower energy was observed with added Mn^{+3} (Nachtegaal, 2003). This was interpreted with partial oxidation of Mn (Nachtegaal, 2003).

3.3.2. *Interaction of Black C with Nonpyrogenic C and Minerals*

Black C is a recalcitrant form of organic C in soils that originates from incomplete combustion of organic matter (Preston and Schmidt, 2006). It is present in soil as finely divided particulates with a large surface area. Typically, nonblack C is found associated with black C particles as shown *in situ* by NEXAFS studies using STXM (Lehmann et al., 2005). Such interactions between nonblack C and black C appear to have quantitative importance (Pietikäinen et al., 2000), but the mechanism of the interaction has not been studied in detail. Similar to the study of interactions between minerals and organic C, NEXAFS may provide an opportunity to provide insight into the nature of the black C interaction with nonblack C. The strength of NEXAFS lies in the ability to distinguish between black C and nonblack C on the basis of both morphological and bond characteristics (Lehmann et al., 2005; Liang et al., 2006).

For the study of interactions between black C and minerals, similar constraints apply as discussed above for nonblack C and minerals. Again, multielement approaches using NEXAFS for the investigation not only of the distribution of element contents, but their chemical form, will allow significant advances in this area. Figure 10.7 shows C *K*-edge NEXAFS images of a black C particle in relation to Ca $L_{3,2}$-edge and Fe L_3-edge NEXAFS spectra near its surface. Black C can be clearly distinguished from nonblack C on the basis of its high aromatic C contents (Fig. 10.7). Nonblack C close to black C surfaces appears to bear greater peak intensities at 287.3 eV attributable to aliphatic C compounds, whereas nonblack C with increasing distance to the black C surface shows stronger peaks at 288.1 eV, which is suggestive of carboxyamide compounds. Similar to interfaces between minerals and organic C, spectral distortions due to high or changing optical density should also be considered. If confirmed, such a finding may for example indicate prevalence of less oxidized material toward black C surfaces covered by more oxidized microbial matter. Spectral signatures of Ca resembled carbonaceous Ca in the black C particle, with slightly changing spectral features in regions of nonblack C with smaller pre-edge peaks possibly from Ca associated with polysaccharides (Obst et al., 2007).

3.4. Carbon Chemistry in Micropores

The mineral matter of soils generally comprises micro- and mesoporosity (De Mayer et al., 2004; Jonge et al., 2000; Mayer, 1994). However, the importance of micro- and mesopores for organic C stabilization is unclear. Mayer (1994) introduced the concept by which organic C contained in pores is protected against microbial decay, because microorganisms and their extracellular enzymes are excluded due to their size. Theories of how organic C is stabilized in soil provide models that shape our understanding of the nature of C in pores. Encapsulation of weakly altered plant material into macroaggregates (Tisdall and Oades, 1982) should result in chemical signatures of pore-oriented organic C reminiscent of plant organic C. This has indeed been amply demonstrated by using a combination of

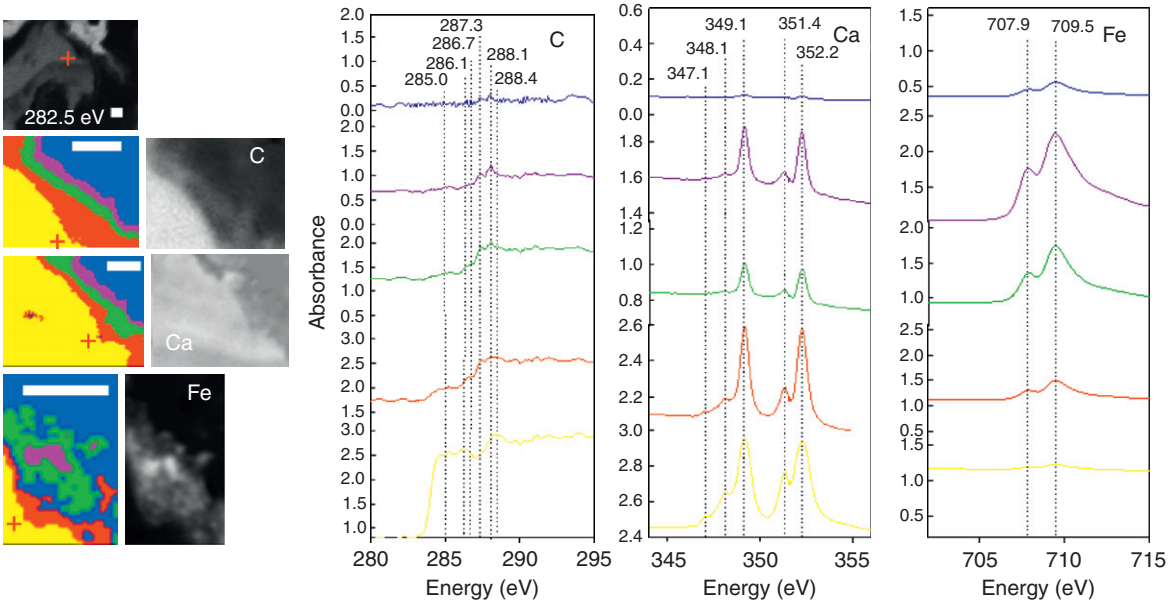

FIGURE 10.7 Carbon (C), calcium (Ca), and iron (Fe) NEXAFS spectromicroscopy of the interface between a black C particle and other soil C and mineral matter. Upper left, optical density of the black C particle environment at 285.2 eV; below, pairs of cluster maps (left) and difference maps of C (subtraction of 280 to 282 eV from 290 to 292 eV), Ca (344-346 eV from 352 to 353 eV), and Fe (700-704 from 707 to 711 eV); right, spectra with colors corresponding to areas in the maps. White bar indicates 1 μm; red cross indicates same position in the different maps (measured at beamlines X1A1 at NSLS (C) and 10ID-1 at CLS (Ca, Fe)).

aggregate and density fractionation to separate light organic matter after destruction of aggregates by sonication (Six et al., 1998; Sohi et al., 2001). Physical fractionation may be less successful in achieving the same distinction for microaggregates, where the difference between adsorption of organic matter to mineral surfaces and pore orientation is blurred due to the small sizes of pores (Lehmann et al., 2007). Important insight can be gained by adsorption experiments that test organic C preservation in micro- and mesopores (Kaiser and Guggenberger, 2003; Zimmerman et al., 2004). Blanco-Canqui and Lal (2004) discussed how the development of models will facilitate better understanding of C sequestration in soils. However, since most conceptual models are built on evidence collected from destructive SOM tests, they fail to explicitly provide a linkage to spatial functionality of C stabilization occurring in microaggregate pore regions (Kinyangi et al., 2006). This shortcoming is attributed in part to the slow advancement of methodological approaches addressing the functional relevance of SOM (Elliott et al., 1996; Sohi et al., 2001; Wander, 2004). Although progress in scanning electron microscopy (Kaiser and Guggenberger, 2006; Mikutta and Mikutta, 2006; Mikutta et al., 2004), computer microtomography (Albee et al., 2000), atomic force microscopy (Kaiser and Guggenberger, 2006), and X-ray scattering techniques (Amelung et al., 2002; Leifeld and Kögel-Knabner, 2003; Weidler et al., 1998) now render images of internal microaggregate porosities and their intra-aggregate C attributes, the spatial interrelationship between soil organic C functionalities and aggregate stability are still largely unknown.

Application of synchrotron-based spectromicroscopy to study the structure of biomaterials (Hitchcock et al., 2002) now affords the opportunity to adapt novel techniques to investigate nanoscale processes in C chemistry and structural assembly of soil aggregates. Recent attempts by Schmidt et al. (2003) show that spectromicroscopy can be used to capture the microscale variability of SOM in hydrated soil samples dispersed in aqueous media. In an attempt to elucidate the surface C functional characteristics of 5-80 mm size black C particles, Lehmann et al. (2005) succeeded in preparing 200 nm thin black C sections for X-ray microscopy and spectroscopic imaging. In this approach, a combination of STXM is used in conjunction with NEXAFS to study the nanoscale distribution of C forms on particle surfaces in soil. Multiple C 1s electron transitions in the NEXAFS region (284-290 eV) reveal the presence of C moieties such as aromatic-C (C=C), aliphatic-C (C-H), carboxyl-C (COOH), and carbonyl-C (C=O). Using similar approaches, Kinyangi et al. (2006) examined the structural features that confer stabilization of C in the microaggregate soil assemblage and resolved the nanoscale spatial distribution of organic C functional forms on surfaces and interior regions of soil microaggregates for the first time. These authors found that the organic matter inside pores of this size have greater proportions of aromatic and aliphatic C, whereas coatings of minerals showed more carboxylic or carboxyamide C (Fig. 10.8). Greater proportions of carboxylic/carboxamide C associated with mineral surfaces than bulk soil C properties were also reported by Lehmann et al. (2007).

3.5. Microbial Habitat and Environment

NEXAFS presents a unique opportunity to map the chemical environment of microbial habitats in soil. The ability to potentially distinguish between microbes themselves and microbial metabolites, enzymes, or the functional group chemistry of live and dead microorganisms may significantly enhance our understanding of microbial ecology and functioning in soil. Spectra for bacteria and fungi isolates from soil show characteristic peaks at 288.4 eV and 289.6 eV, respectively (Liang et al., 2006). To the best of our knowledge, no information has been published to date that shows C

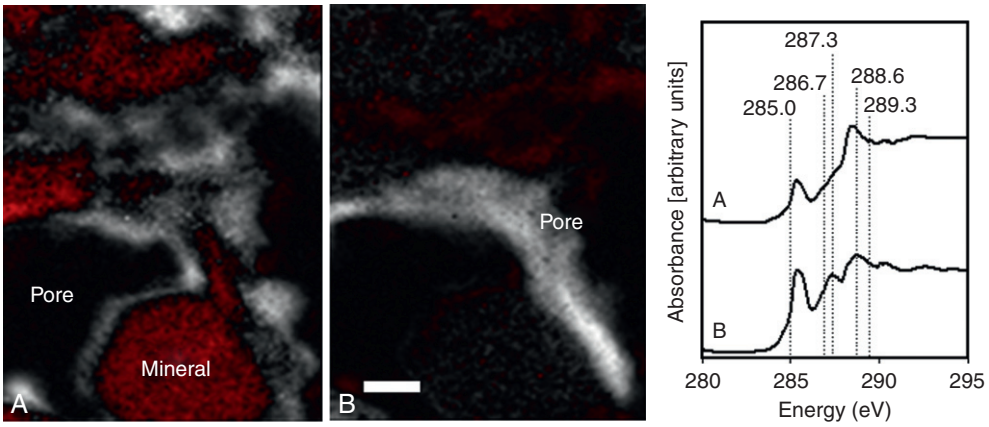

FIGURE 10.8 Singular value decomposition of spectral properties of C forms determined by NEXAFS spectroscopy and STXM of a micrometer size pore (recalculated after Kinyangi et al., 2006). Areas with white color in images are characterized by the associated spectrum with the same letter. White bar indicates 1 μm.

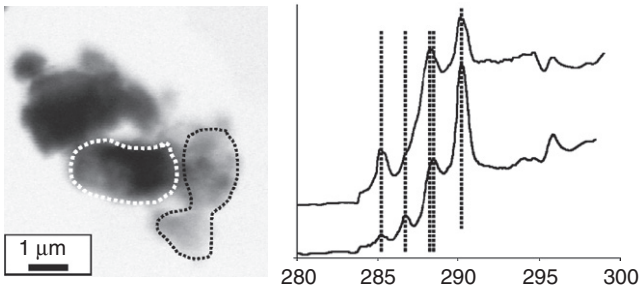

FIGURE 10.9 Carbon *K*-edge NEXAFS analysis of microbial matter of a sediment sample obtained from Lake Van (eastern Turkey). Image was taken at 288.2 eV. (A) and (B) correspond to the regions within the sample for which full spectra are shown on the right. Dashed lines correspond to (from left to right) energy positions of 285.2, 286.8, 288.2, 288.6, and 290.2 eV (changed after Benzerara et al., 2006; with permission from the publisher).

NEXAFS and STXM data of microorganisms *in situ* in soils. More information is available about microorganisms in lake sediments (Benzerara et al., 2005, 2006), in river water (Hitchcock et al., 2005; Lawrence et al., 2003), or in flooded underground tunnels of mines (Chan et al., 2004).

Bacteria typically show a characteristic peak at an energy of 288.2-288.4 eV, indicative of peptide C with no other peak than that of aromatic C (Benzerara et al., 2006; Liang et al., 2006). These peak positions of 288.2-288.4 eV are slightly lower than those observed in organic matter extracts from soil (Solomon et al., 2005, 2007a), in soil microaggregate regions not associated with microorganisms (Kinyangi et al., 2006; Lehmann et al., 2007), and total soil (Lehmann et al., 2008), which typically lie between 288.6 and 288.7 eV. In lake sediments, a shift toward higher energy positions from 288.2 to 288.6 eV was interpreted as extracellular polymeric substances surrounding bacteria (Fig. 10.9; Benzerara et al., 2006). This interpretation was based on analyses of peptide compounds (Lawrence et al., 2003) and hydroxamate C (Edwards and Myneni, 2006) that show $1s \rightarrow \pi^*$ transition at 288.2 eV.

4. PROSPECTS FOR FUTURE RESEARCH

Research to date has clearly shown the strength that synchrotron-based spectroscopy possesses for the investigation of soil organic C. This strength is primarily based on the ability of synchrotron radiation to allow (1) better spectral quality for samples with low C concentrations as is typical for soil and (2) measurements obtained with high spatial resolution. Results demonstrate that composite analyses of the total soil organic C have significant limitations in giving information about actual compounds present in soil. Given the pronounced spatial complexity of organic C forms that may be affected to different extends by microorganisms, minerals, and pore spaces, spatially explicit information may be an important building block to improve our understanding of soil organic C processes. On the other hand, such spatially detailed mapping of organic C also poses challenges when information on single locations needs to be scaled to processes observed at the pedon or landscape scale.

In addition, significant constraints need to be considered that may partly be resolved in the future, such as sample preparation, control of radiation damage, or spectral quantification. The data from spectral information of standard substances is still insufficient to fully identify functional group chemistry for soil organic C and a concerted effort is required to fill that gap as soon as possible. The application of information derived from standards to soil organic C is only beginning and requires careful consideration of the changes in spectral properties induced by pH, cation and anion activity, or mineral admixture.

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