Chemical Characterization of Black Carbon Reference Standards Using C 1s NEXAFS Spectroscopy

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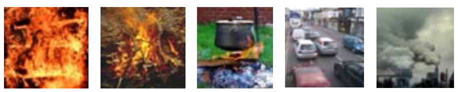
Introduction

- We utilized carbon (C) Near Edge X-ray Absorption Spectroscopy (NEXAFS) to characterize C composition of black carbon (BC) reference materials (Hammes, 2008)
- BC represents a range of residues from biomass burning and fossil fuel combustion (Schmidt, 2002)
- BC is ubiquitous in terrestrial ecosystems due to deposition and burning events over time
- BC is highly stable form of C on millennial time scale, chemistry may control longevity
- Participates in global biogeochemical cycles, pollutant fate, therefore, impacts are far reaching



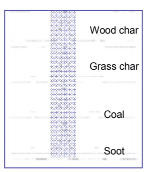
Combustion Continuum

	slightly charred biomass	char	charcoal	soot	GBC
Formation temperature	low--→high				
Size	------mm and larger------mm to submicron-----submicron				
Plant structures	abundant	significant presence	few	none	
Reactivity	high---→low (inert)				
Initial reservoir	soils		soils and atmosphere		

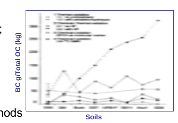
Table 1. The combustion continuum describes range of BC characteristics (Masiello, 2004)

Anthropogenic soil profile rich in 130 yr old charcoal

NEXAFS improves upon current BC characterization methods by capturing total carbon; preserves structural integrity of samples…no destructive sample processing required



- The combustion continuum illustrates structural differences among BC types
- However, differences among highly aromatic BC not detectable with ^{13}C Nuclear Magnetic Resonance (NMR) due to lack of protons within the molecular matrix of black carbon
- Schmidt et al. (2002) compared different chemical and thermal quantification methods for measuring BC concentrations in soils; however, methods yielded highly variable results
- Developing methods such as NEXAFS:
  - Will improve non-destructive characterization of BC
  - Develop the technology for accurate BC quantification
  - Provide comparative analysis for other spectroscopic methods



Objectives

- Our objective was to chemically characterize the C edge of BC reference materials
- Identify characteristics to separate a BC signature from environmental matrices
- Distinguish unique characteristics of BC versus potential interference materials
- Develop NEXAFS as a viable characterization tool for soil and environmental science
- Expand the toolbox of currently available characterization and quantification methods utilized for BC

Methods and Materials

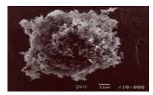


Table 2. BC reference materials

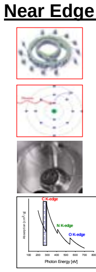
N-hexane soot (ST) Grass char (rice straw) (GC) Wood char (chestnut) (WC)
Urban dust (aerosol) (UD) Marine sediment (MS) Vertisol (clayey soil) (VT) Chernozem (sandy soil) (CH) Dissolved OM (DOM)
Melanoidin (MEL) Shale (SH) Bituminous coal (BIT) Lignite coal (LIG)

BC reference standards*

- Enriched carbon materials (BC) were produced in laboratory under controlled conditions
- Environmental matrices known to contain BC were collected
- Materials known to interfere with BC extraction and analysis were obtained

***more information: www.geo.unizh.ch/phys/bc/**

Near Edge X-ray Absorption Spectroscopy (NEXAFS)



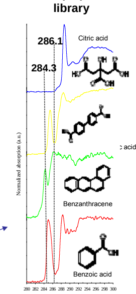
What is a synchrotron?

- When high speed, high energy electrons are accelerated or their path is bent in passing through powerful magnetic field, a natural phenomenon occurs to produce brilliant full spectrum beams of photons known as synchrotron light
- Light 1 million times brighter than sunlight!...Produces IR, UV and X-ray light
- Allows scientists to investigate the relationships between atoms in a molecule
- Monochromators select for specific elements such as C, N, O, P, S

Why NEXAFS for black carbon?

- Probes electronic state of solid samples through inner shell excitation processes
- At photon energies close to an atomic absorption edge, the inner shell e^- excited to unoccupied energy level, creating resonance peaks in absorption region (Stohr, 1992)
- Advantage of mounting solid samples on sample holders without chemical or thermal pretreatment, which can alter sample structures
- Method is considered quantitative for C, no bias against certain forms
- Useful for C rich samples which are difficult to quantify with other methods
- Chemical standards are measured with NEXAFS to establish a spectral library for identification of functional groups in chemically heterogeneous materials such as BC

Chemical reference standards used to develop spectral library



Data analysis

Fig. 1. Deconvolution of NEXAFS spectra using 8 Gaussian curves with area under curves corresponding to % total C

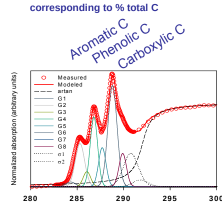


Table 3. Approximate energy ranges of primary absorption peaks at C (1S) edge

Functional group	Examples	Bond	Transition	Peak energy (eV)
Aromatic-C	Quinone-type-C Protonated and alkylated aromatic-C Heteroatom-substituted aromatics	C=O	1s-π*	283.0-284.5
Aromatic-C	Protonated and alkylated to carbonyl-substituted aryl-C Pyrimidic-C Olefinic-C	C=C	1s-π*	285.0-285.5
Phenolic -C	O-substituted aryl-C and ketonic-C Phenyl-C attached to amide group	C-OH C-O C=O R-(C=O)-R'	1s-π*	286.0-286.7
Aliphatic-C	Aliphatic-C of CH_3, CH_2 and CH nature	C-H	1s-3p/σ*	287.0-287.6
Carboxylic-C	Carboxylic-C Carboxyamide-C	COOH -COO C=O -(NH2)-C=O	1s-π	288.0-288.7
O-alkyl-C	Polysaccharides, alcohols and ether-C	C-OH	1s-π	298.2-289.5

Results

1. NEXAFS Spectra:

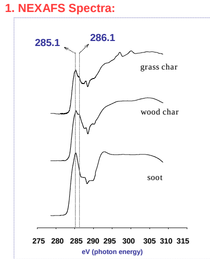


Fig. 2. NEXAFS spectra of carbon rich standards

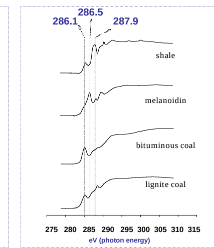


Fig. 3. NEXAFS spectra of potential interference materials

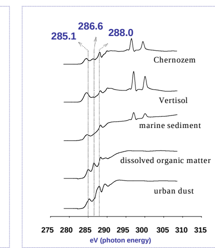


Fig. 4 NEXAFS spectra of environmental BC matrices

2. Spectral deconvolution

eV	G1 284.5	G2 285.4	G3 286.1	G4 286.7	G5 287.9	G6 288.4	G7 289.4	G8 289.7	O-alkyl C/ Aromatic C
WC	18.30	22.37	8.54	20.28	18.12	1.85	5.09	5.45	0.15
GC	12.60	21.80	14.37	12.11	18.65	8.36	8.12	3.99	0.20
ST	22.49	20.61	7.88	11.49	16.44	9.24	6.81	5.05	0.19
UD	2.69	14.46	1.86	11.91	24.70	10.02	26.94	7.42	1.11
SH	1.55	11.84	1.11	9.21	36.22	18.99	5.06	16.03	0.89
DOM	6.39	10.06	7.37	17.32	13.42	13.82	17.79	7.90	0.62
MS	9.62	8.87	5.85	10.38	16.17	29.06	4.28	15.77	0.58
LIG	7.89	13.23	8.52	12.22	13.31	20.67	9.64	14.52	0.58
BIT	13.32	24.95	2.59	11.30	17.93	14.26	10.21	5.44	0.30
MEL	5.64	11.14	15.77	20.14	15.90	5.00	15.64	10.76	0.50
VT	20.26	11.41	6.19	7.51	9.86	19.95	5.93	18.88	0.55
CH	11.35	11.08	4.54	13.07	13.05	23.82	13.28	9.80	0.58

Table 4. Spectral peak areas determined by deconvolution using 8 Gaussian peaks and arctangent step function

Fig. 5. Aromatic C (% total C) taken as G1+G2 curves

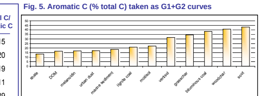
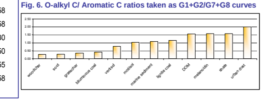


Fig. 6. O-alkyl C/ Aromatic C ratios taken as G1+G2/G7+G8 curves



3. Comparison of NEXAFS O-alkyl C/aromatic C ratio results with ^{13}C NMR O-alkyl C/aromatic C ratio (Hammes et al., 2008)

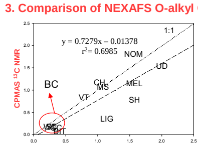


Fig. 7.

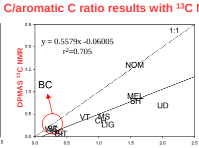


Fig. 8.

- **Data points (Fig. 7, 8)are coordinates of ^{13}C NMR and NEXAFS ratios**
- **There was a positive correlation between the data**
- **We expected data points to fall on 1:1 line with perfect agreement between the two data sets**
- **We expected data points to fall above 1:1 line if NEXAFS improves detection of aromatic C**
- **We observed the inverse of what we expected; however, we attribute this to overlooked errors in the accepted data processing methods, and not to the instrumentation**

Conclusions

- NEXAFS spectroscopy is a powerful method for examining the chemical composition and functional diversity of BC
- Spectra distinguished the fine structural details of BC and differences among different BC types
- NEXAFS spectra provided evidence that BC is chemically distinct from potential interference products
- Positive correlation with ^{13}C NMR data make NEXAFS a very useful addition to the spectroscopic toolbox
- Data analysis using peak fitting and arctangent step functions must be improved to give better fits to C spectra

Outlook: NEXAFS will be an exciting tool for carbon quantification of BC, soils and sediments

References
1. Hammes et al., 2008, *Applied Geochemistry* Vol 23: (8) 2113-2122
2. Masiello, 2004. *Marine Chemistry* Vol 92: 201-213
3. Schmidt et al., 2001, *Global Biogeochemical Cycles* 15: 163-167
4. Stohr, J. (Springer, 1992)

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