Mineralogical controls on soil black carbon preservation

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1. Introduction

Black carbon (BC) has long been considered a chemically resistant component of soil organic carbon (SOC). However, there is substantial evidence that the chemistry of most C compounds is less important for long-term storage than is physical protection (e.g., mineral sorption). We explored BC retention in grasslands that lie along a climate gradient that produces strong differences in short range order (SRO) minerals known to drive landscape-scale retention of SOC. We measured soil BC content using 13C nuclear magnetic resonance (NMR) spectroscopy, and used radiocarbon dating on a subset of samples to relate BC content to long-term soil C storage. Black C concentrations in soil ranged from 0.2 to 2.9%, representing 10–30% of SOC and spanning levels found in temperate grasslands around the world. Black C concentrations were significantly correlated with SRO minerals, but the strongest single predictor of BC content was simply SOC. The ratio of BC/OC was fairly insensitive to SRO minerals, suggesting that BC responds similarly to reactive minerals as does OC. Direct links between SOC and BC retention warrant further study. We found no evidence that BC is preferentially retained relative to OC, with soil radiocarbon ages apparently driven primarily by inputs of new OC. These results indicate that physical protection may play a strong role in BC retention, and that BC cycling in soils may be more similar to OC cycling than is generally thought.

associated with SRO mineral concentrations along the Hawaiian gradient, and C turnover times are slowest where concentrations of these minerals are highest [Torn et al., 1997].

[5] To address our hypothesis we combined a broad-scale correlative approach examining relationships between BC and soil mineralogy across the gradient, and radiocarbon dating of soils with different concentrations of BC. If physical protection is important for BC storage, then the ratio of BC/OC versus SRO minerals should be relatively constant, indicating that BC and OC are equally likely to undergo organo-mineral interactions. In this case, BC should not be significantly older than bulk soil C, such that soil C age would not be related to BC content of soils, and the BC/OC ratio would also be constant relative to soil radiocarbon age. Alternately, if BC storage depends primarily on its inherent chemical recalcitrance, then the ratio of BC/OC versus SRO minerals should be negative, indicating that OC is more mineral-reactive than BC. If BC were preferentially retained, then increased BC content of soils should drive older soil radiocarbon ages. While this approach does not provide direct measures of mechanisms, a strong correlation between SRO minerals and BC in this well-characterized system would suggest that BC is more reactive than generally assumed, and that its storage in soil may be subject to similar controls as OC.

2. Methods

2.1. Overview of Approach for Quantifying BC

[6] Black C spans the morphological range from microscopic soot to large wood charcoal; its abundance is notoriously difficult to quantify in mineral soil, with most common methods likely missing some portion [Hammes et al., 2007]. Difficulties include random or biased losses of C groups during BC purification/isolation procedures, mis-identification of other C compounds as BC, and/or creation of new BC during the BC isolation procedures. In most quantification methods, the soil matrix surrounding BC is lost or altered, making it difficult to directly observe associations of BC with minerals or other OM. Direct observation of BC in the soil matrix is possible via microscopic methods, but not in a quantitative way.

[7] We used a spectroscopic method based upon direct polarization (DP) 13C nuclear magnetic resonance (NMR) to quantify BC in soils. DP 13C NMR is the most quantitative tool available for the structural characterization of BC because it directly measures bridgehead C at the molecular scale rather than a proxy or marker, and thus it captures the broadest range of BC structures [Fang et al., 2010]. In contrast, the cross-polarization (CP) technique underestimates the aromatic bridgehead carbon present in BC [Preston and Schmidt, 2006]. Nevertheless, DP 13C NMR used alone does not have the ability to resolve BC-derived aromatic carbon from aromatics in lignin or other biomolecules. In some studies, this problem is overcome with a pretreatment step designed to remove an operationally defined fraction of non-BC SOC based upon susceptibility to thermal, chemical, or photolytic oxidation. An alternative approach uses spectral editing to separate BC from aromatic biomolecules based upon the presence of protonated aromatic C or differences in the aromatic proton relaxation rate [Fang et al., 2010; Smernik et al., 2000]. Both of these approaches involve operational definitions of BC. The third approach, applied here, uses a matrix of linear equations to attribute the functional groups observed by NMR to constituents of SOC using a molecular mixing model [Baldock et al., 2004].

[8] The molecular mixing model iteratively determines the linear combination of six major SOC constituents (BC, carbohydrate, lignin, lipid, protein, and carbonyl) that best fit the integrated regions of the NMR spectra [Baldock et al., 2004]. For example, aromatic carbon in general contributes to the 13C NMR aromatic peak intensity at 130 ppm (Figure S1 in the auxiliary material), but condensed aromatic carbon atoms in BC can be separated from single aromatic rings present in biological molecules (lignin or protein) because the latter also contribute to spectral intensity at 56 and 150 ppm [Garny et al., 2010; Krull et al., 2006]. Tannins are not a quantitatively important component of the carbon pool [Adamczyk et al., 2009; Hernes and Hedges, 2000], and therefore, are not considered in the mixing model. If present, tannins would be partitioned into the lignin and carbohydrate classes by the mixing model based on the distribution of C functional groups. Thus, the mixing model is particularly useful for accurately separating the condensed aromatic C in BC from other aromatic C.

[9] Historically, humic material was thought to consist of large polymers containing aromatic compounds created via condensation reactions during microbial decomposition [Stevenson, 1994]. These super-molecules were thought to contribute newly synthesized aromatic structures to soils, which would be difficult to distinguish using the molecular mixing model. However, the importance of these reactions and the neoformation of super-molecules has been questioned [Sutton and Sposito, 2005]; recent analyses suggest that alkali-extractable SOC is dominated by biological molecules in various stages of decomposition that differ in their propensity for metal complexation, micelle formation, and non-covalent interactions [Kelleher and Simpson, 2006; Lehmann et al., 2008; Sutton and Sposito, 2005]. If this model of SOC is valid, the six components in the mixing model should accurately represent the mixture of biomolecules present in soil.

2.2. Study Site

[10] The rainfall and soil weathering gradient used in this study is on the leeward side of Kohala Volcano on the Big Island of Hawaii (20.15 N, 155.83 W), and includes basaltic lava flows of two different age ranges. Rainfall ranges from 220 to 2400 mm MAP, with soil weathering status positively associated with precipitation [Chadwick et al., 2003; Porder and Chadwick, 2009]. Short range order mineral content increases with rainfall up to about 2000 mm MAP [Chadwick and Chorover, 2001; Chadwick et al., 2003]. Precipitation covaries strongly with soil physical and chemical properties along the gradient. Soil from the two ages of lava flows, a younger (0.23 to 0.12 Ma: Hawi) [Spengler and Garcia, 1988] and an older formation (0.46 to 0.26 Ma: Pololu) [Chadwick et al., 2003] were used to maximize variability in SRO mineral concentration.

1Auxiliary materials are available in the HTML. doi:10.1029/2011GB004109.
[11] Pre-contact vegetation for the site was mixed C3 trees and C4 grass understory, with grasses declining in importance at higher rainfall [Chadwick et al., 2007]. Currently, Buffel grass (Cenchrus ciliaris) and the tree keawe (Prosopis pallida) are dominant below 750 mm MAP, and pastures with kikuyu grass (Pennisetum clandestinum) dominate from 750 to 2,000 mm MAP [Pratt and Gon, 1998]. Wildfire frequency in the native ecosystems was low, although cooler and drier climates in the past supported Pleistocene-era fires in parts of Hawaii [Hotechkiss et al., 2000]. Polynesians cultivated part of the gradient from ~700 to 1,700 mm MAP between 1400 to 1800 A.D., introducing crop plants and likely increasing fire frequency [Allison and Vitousek, 2004; Kirch et al., 2004]. In the 19th century ranchers expanded land clearing and introduced pasture grasses from Africa. The spread of these and other exotic grasses has greatly increased fire frequency, intensity, and expance in the landscape since the 1930s. The Hawaiian Wildfire Management Organization (HWMO) has mapped wildfires on the Island for the past 100 years, showing that the majority of modern wildfires have occurred in areas with less than 1000 mm of rainfall per year [Smith, 2010]. While modern fires are concentrated in lower rainfall areas, a high incidence of wildfires to the south and sugarcane burning to the east of Kohala and the very fine texture of grass charcoal, make deposition of modern BC across the landscape extremely likely [Kuhlbusch et al., 1998; Rodionov et al., 2010]. Although quantitative information about BC inputs to these soils is lacking, we assume that it is relatively uniform across the rainfall gradient, and we address the implications of that assumption below.

2.3. Soil Sampling

[12] The sampling transects used for this study avoided areas of wildfire mapped by the HWMO in an attempt to measure only general landscape-scale levels of BC rather than immediate effects of fire. We collected soil from one transect on each geological formation (substrate age), with most of the sampling area in active pastures. Soil was collected from 0–30 cm from pits along each transect, with 34 sites on the younger lava flow and 16 on the older lava flow. Samples were air-dried, sieved to 2 mm, and ground in glass vials using a jar mill.

[13] Soil bulk density was measured in six pits on the younger lava flow and seven pits on the older lava flow, spanning the precipitation gradient. Bulk density was measured on soil clods collected behind the face of soil spanning with water displacement after the clods were coated with liquid polyvinyl chloride (i.e., Saran) [Blake and Hartge, 1986]. For both geological formations, bulk density declined significantly and linearly with precipitation (\(R^2 = 0.75\) for Hawai, \(R^2 = 0.83\) for Pololu). To calculate soil C and BC stocks at sample points between pits on each geological formation, bulk density values were interpolated using a linear regression.

2.4. Soil Mineralogy and Chemistry

[14] Short range order minerals (primarily allophane and ferrihydrite) were measured as an indication of soil capacity for physical protection of SOC along the gradient. We used an ammonium oxalate extraction [Parfitt and Henmi, 1982] with modifications as noted. Approximately 0.5 g of soil dried under vacuum at 60°C was extracted in 30 mL of 0.2 M ammonium oxalate solution (pH 3), put on a shaker in the dark for 4 h, and centrifuged. The supernatant was decanted and the remaining pellet was dried under vacuum at 60°C until weight stabilized. The difference between initial and final weight was used as the total SRO mineral content (i.e., acid-oxalate extractable). Other characteristics of soil from the gradient were measured as potential covariates, including cation exchange capacity (CEC), resin phosphorus (P), extractable base cations, and total elemental composition (percentages by weight) using the procedures in Allison and Vitousek [2004].

2.5. Black Carbon Quantification
2.5.1. Hydrofluoric Acid Treatment

[15] For optimal \(^{13}\)C NMR performance mineral and glass fractions were removed from soil using hydrofluoric acid, which also concentrates SOM, improving spectroscopic characterization of C [Schmidt and Gleixner, 2005; Schmidt et al., 1997]. The pre-treatment with hydrofluoric acid causes some loss of C, which is the greatest drawback of using \(^{13}\)C NMR to quantify SOC in mineral soil. However, lost C is most likely comprised of acid-soluble, low-molecular weight compounds, and losses of BC are unlikely. We measured soil C content at all steps of the hydrofluoric acid pre-treatment protocol to track C losses. Soils were treated with hydrofluoric acid following the methods in Gélinas et al. [2001] with changes as noted. Approximately 5 g of soil were dried at 60°C under vacuum and then gently shaken in 1% HCl to remove CaCO₃. The floatable fraction of soil was decanted and saved. This initial step was done in duplicate, and one duplicate was used to account for CaCO₃-C lost via CO₂ off-gassing, and the C content of the floatable fraction. The other duplicate was then shaken with 10% v/v hydrofluoric acid in 1 N HCl for 24 h, repeated three times. The resulting soil pellets were rinsed with deionized water three times. Floatable fractions and soil pellets were dried under vacuum at 60°C, weighed, and ground with a mortar and pestle. Bulk soils (pre- and post-treatment) and floatable fractions were analyzed for C and nitrogen (N) on a Fisons/CE NA 1500 Series 2 Elemental Analyzer using alanine as a standard.

2.5.2. \(^{13}\)C NMR Spectroscopy and Mixing Model

[16] Direct polarization \(^{13}\)C NMR was conducted on 200 MHz (Rice University; Houston, TX), and on 300 MHz (University of California - Santa Barbara, CA) Varian/Chemagnetics Infinity CMX nuclear magnetic spectrometers (Varian NMR, Fort Collins, CO). Magic angle spinning (MAS) frequency of 7 kHz was used on the 200 MHz spectrometer, and 10.5 kHz spinning frequency on the 300 MHz (resulting in the same spinning sideband distribution) in 5 mm HXY MAS probes. Approximately 60 mg of treated soils were packed in 4 mm (outer diameter) zirconia rotors sealed with a Kel-F cap (Bruker BioSpin, Billerica, MA). Spectra were acquired following a 30 degree \(^{13}\)C excitation pulse with a 5 s recycle delay between acquisitions, two-pulse phase-modulation (TPPM) decoupling, and a pulse length of 1.2 μs. A spectral width of 803 ppm was used, and the number of scans ranged from 1800 to 10,500 to maximize signal:noise ratios for each sample. The combination of pulse length and delay time were selected for
quantitative detection of charcoal based upon preliminary spin counting measurements on charcoals produced in the lab at a wide range of pyrolysis temperatures.

[17] We used direct polarization $^{13}$C NMR with dipolar-dephasing to quantify the non-protonated aromatic C (110–145 ppm). This metric can be used as a conservative measure of BC [Fang et al., 2010] because it excludes protonated aromatic; therefore, it excludes BC surface groups. We applied this approach to four samples as an independent check of BC values determined by DP $^{13}$C NMR and the molecular mixing model. Dipolar-dephasing NMR spectra were collected using the same parameters as DP $^{13}$C NMR, with the addition of a 50 µs dephasing delay, which we found adequate to eliminate the signals from protonated C atoms in both aromatic and aliphatic model compounds. The abundance of aromatic bridgehead C in SOC is viable as a proxy for BC [Fang et al., 2010], because few biogenic molecules contain fused aromatic ring structures (condensed tannins are the only notable exception) wherein non-protonated and non-polar aromatic bridgehead C comprise a majority of the aromatic C present.

[18] Spin counting was conducted to quantify the C detected in the NMR experiment. Our spin counting results indicate that DP $^{13}$C NMR detected 74 ± 5% of the carbon in each soil sample (n = 44). Spinning sidebands were accounted for as in Smernik and Oades [2001b]. A background (empty rotor) signal was subtracted from the spectra to remove signals arising from C in the NMR probe and rotor [Smernik and Oades, 2001a]. The chemical shift (i.e., resonance frequency) of the spectra was referenced to adamantane as an external standard. Spectra were digitally processed with 100 Hz line broadening, a Fourier transformation, exponential apodization, and phase correction on Spinsight 4.2.1 software (Varian NMR, Fort Collins, CO).

[19] This procedure compares the C-normalized signal intensity detected in each sample to the C-normalized signal intensity of a well-characterized external standard [Smernik and Oades, 2000], in this case pure cellulose (Sigmacell cellulose type 101, Sigma-Aldrich).

[20] Peak areas were integrated within seven discrete chemical shifts regions for input to the molecular mixing model: 0–45 (alkyl), 45–65 (N-alkyl/methoxyl), 65–95 (O-alkyl), 95–110 (di-O-alkyl), 110–145 (aromatic), 145–165 (phenolic), and 165–220 ppm (amide / carboxyl) (according to Baldock et al. [2004]) (example spectra in Figure S1, integrated peak areas and molecular mixing model results in Table S1). The molar N:C ratio of each sample was used to constrain the protein concentration in the molecular mixing model. Molecular mixing model fits for all six biomolecules were compared to models eliminating one to three components; in all cases the model fit was best when including all six components, describing >95% of peak area distributions (i.e., sum of squares of deviation < 5%). In total, 44 hydrofluoric acid-treated soils were analyzed using DP $^{13}$C NMR.

2.6. Radiocarbon ($^{14}$C) Dating of SOM

[21] To assess the relationship between BC levels and long-term soil C storage, a subset of ten bulk soils with varying BC content were measured for $\Delta ^{14}$C at the Center for Accelerator Mass Spectrometry (CAMS) at Lawrence Livermore National Laboratory following sample graphitization. Fraction modern (FM) radiocarbon values were corrected for background and $\delta ^{13}$C before calculating radiocarbon age in years before present (BP) [Stuiver and Polach, 1977].

2.7. Statistical Analyses

[22] To explore the relationships between BC and soil mineralogy, we ran a series of analyses of covariance (ANCOVA) using soil BC concentrations, BC content, and the ratio of concentrations of BC/OC (i.e., relative abundance of BC) as response variables. Organic C was calculated simply by subtracting BC from total soil C. Model factors included soil SRO mineral content, CEC, C and N concentrations, soil chemistry, and geological formation. Rainfall was included as a covariate in all analyses. Similar analyses were run using total SOC and other biomolecules from the molecular mixing model as response factors for comparison with trends for BC. For significant factors, post-hoc regressions or Fisher’s Least Significant Difference (LSD) test were used. Analyses were performed using 8.0.2 JMP software (SAS Institute Inc., 2009). Unless otherwise noted, statistical significance for all tests was p < 0.05, and means are reported ± one standard error.

3. Results

3.1. Black C Method Validation/Data Quality

3.1.1. Acid Pretreatment C and N Recovery

[23] As expected, the pre-treatment with HCl and hydrofluoric acid led to some losses of C and N from initial bulk soil, as well as the intended loss of soil mass (mineral fraction) and concentration of C and N in the remaining sample. All C and N lost during the HCl treatment was either in a floatable fraction, or released as CO$_2$ from carbonate dissolution. The loss of C to CO$_2$ off-gassing accounted for 0.6 ± 0.1% (n = 22) of soil mass. The HCl treatment removed an average of 14.5 ± 0.01% of total soil mass (n = 54) during the decanting of the floating fraction. Including the floating fraction of soil, the total mass recovery from the HCl treatment was 99 ± 1% (n = 23). In these soils, with abundant SRO minerals of low density, the floatable fraction was not significantly higher in C and N relative to the dense fraction (i.e., not richer in organic matter), as is generally the case for low density soil fractions [Trumbore and Zheng, 1996].

[24] After hydrofluoric acid treatment, an average of 15 ± 1% (n = 44) of soil mass remained, concentrations of N increased from 0.6 ± 0.03% to 3.0 ± 0.1%, and concentrations of C increased from 6.8 ± 0.5% to 28.6 ± 1.3%. Dissolution of some C and N during the hydrofluoric acid treatment is common, especially in soils having a large proportion of organic matter in mineral associations [Gélinas et al., 2001]. In this study, 80 ± 4% of N and 71 ± 3% of C was retained after the hydrofluoric acid treatment step, and total retention after all treatments (including “loss” to the floatable fraction) was 72 ± 4% of N and 63 ± 5% of C (n = 43).

3.1.2. Confirmation of Abundance of BC by Aromatic Bridgehead C

[25] The application of dipolar-dephasing $^{13}$C NMR to 3 soil samples revealed that >30% of the aromatic carbons in the SOC were bridgehead carbons. This implies that at least 30% of the aromatic C in the SOC can be attributed to BC.
For example, bridgehead C calculated from dipolar-dephasing spectra (following Solum et al. [1989]) gave 5.5 and 13.0 mol % bridgehead C for two separate samples, whereas the DP and mixing model approach gave 4.0 and 14.0 mol % BC for the same two samples, respectively, confirming that the DP and mixing model approach appropriately identifies highly condensed C as BC.

3.2. Environmental Gradient Characteristics

Bulk density from 0–30 cm ranged from 0.99 g/cm³ at 220 mm MAP to 0.22 g/cm³ at 2400 mm MAP on the younger geological formation, and 0.74 g/cm³ at 750 mm MAP to 0.39 g/cm³ at 2200 mm MAP on the older geological formation. The older formation had significantly lower base saturation, lower concentrations of all non-hydrolizable base cations except sodium (Na⁺), lower resin P, and lower percentages of total P, total calcium, total magnesium, and total sodium, and higher percent of total iron relative to the younger formation. The two geological formations did not differ significantly for SRO mineral content, CEC, or C and N concentrations or content (Table S1).

Soil C concentrations ranged from 1.4 to 16.3%, and were positively correlated with SRO mineral concentration (Figure 1a, $R^2 = 0.67$, $n = 49$, $P < 0.05$). Rainfall covaried positively with SRO minerals (Figure 1b, $R^2 = 0.56$, $n = 49$, $P < 0.05$), and adding rainfall to the SRO regression did not improve prediction of soil C concentrations. Using bulk density values to calculate soil C stocks, soil C content ranged from 2 to 30 kg/m² across the rainfall gradient. Soil C content correlated positively with SRO minerals ($R^2 = 0.49$, $n = 49$, $P < 0.05$), but the relationship of soil C content with rainfall was weak ($R^2 = 0.12$, $n = 47$, $P < 0.05$). There were no significant differences between the two geologic formations, and chemical characteristics of the two substrates were not significant predictors in any analysis of soil C or BC, so data from both geological formations were pooled for subsequent analyses.

3.3. Black Carbon Distributions

Black C concentrations ranged from 0.2 to 2.9% of soil weight, and BC content ranged from 0.3 to 5 kg/m² across the precipitation gradient (Table S1). The strongest predictor of BC concentrations was OC concentration (Figure 2a, $R^2 = 0.85$, $n = 44$, $p < 0.05$), suggesting a direct relationship between these two C pools. Not surprisingly, factors that correlated with SOC were also correlated with BC concentrations. For example, the second strongest predictor of BC concentrations was SRO mineral content (Figure 2b, $R^2 = 0.46$, $n = 44$, $p < 0.05$), similar to relationships of SRO minerals with other C groups. Rainfall was also a significant but weaker predictor of BC concentrations ($R^2 = 0.21$, $n = 44$, $p < 0.05$, all relationships positive).

The ratio of BC/OC across the gradient ranged from 0.12 to 0.43. This ratio was most strongly correlated with precipitation (Figure 3a, $R^2 = 0.31$, $n = 44$, $p < 0.05$, negative relationship), showing relatively larger pools of OC at higher precipitation, whereas BC pools were relatively constant. The relationship of BC/OC versus SRO mineral concentrations was weak ($R^2 = 0.16$), suggesting that SRO minerals are similarly important for OC and BC retention. In ANACOVA, rainfall was a significant factor for predicting BC/OC ratios, whereas SRO mineral concentrations were not. Even though both BC and OC increased with precipitation, the increase in OC was much larger. The negative relationship of BC/OC with precipitation suggests that either more BC is produced in dry sites, or the preservation of BC is greater in dry sites relative to OC.

3.4. Soil Organic Matter Chemistry

Similar to BC, the concentrations of other biomolecules (carbohydrate, carbonyl, lignin, lipid and protein) were positively correlated with total soil C concentrations ($R^2 = 0.87, 0.53, 0.38, 0.64, 0.90$, respectively, $n = 44$, $p < 0.05$), indicating that drivers of soil C retention affected all C chemical groups. As a proportion of total SOC,
carbohydrates were 20 ± 1%, carbonyl was 18 ± 1%, lignin was 8 ± 1%, lipids were 9 ± 1%, and proteins were 28 ± 1% (Table S1). There were few correlations between environmental factors and the relative abundances (i.e., biomolecule/OC ratios) of biomolecules. Aside from BC, only the ratio of lipid/OC was correlated to rainfall, with higher lipid/OC in wetter sites ($R^2 = 0.18$, $n = 44$, $p < 0.05$). Carbohydrate/OC ratios increased with SRO mineral concentration ($R^2 = 0.29$, $n = 43$, $p < 0.05$). Carbohydrate/OC ratios were weakly correlated with total soil C ($R^2 = 0.16$, $n = 43$, $p < 0.05$), with no similar correlations for other biomolecule abundances, suggesting that carbohydrates may have played a slightly stronger role in increased soil C concentrations and SRO associations than other biomolecules. Still, no single biomolecule emerged as clearly dominant in organo-mineral interactions or total SOC storage.

### 3.5. Soil Radiocarbon Ages

[$^{31}$] Radiocarbon ages of bulk soils declined strongly and logarithmically in relation to OC content (Figure 4a, $R^2 = 0.78$, $n = 10$, $p < 0.05$), with modern radiocarbon signals in the most C-rich sites. Overall, the contents and concentrations of all biomolecules were negatively correlated with soil radiocarbon age, with significant relationships for protein content ($R^2 = 0.67$), BC content ($R^2 = 0.65$), lipid content ($R^2 = 0.51$), and carbohydrate content ($R^2 = 0.50$, $n = 10$, $p < 0.05$ for all). Radiocarbon ages were also negatively correlated to rainfall ($R^2 = 0.63$) and SRO mineral content ($R^2 = 0.70$, $p < 0.05$, $n = 10$ for all). The BC/OC ratio was positively correlated with soil radiocarbon ages (Figure 4b, $R^2 = 0.44$, $n = 10$, $p < 0.05$); this trend appeared to be primarily related to the strong negative relationship between OC concentrations and radiocarbon age, whereas the decline in BC concentrations with radiocarbon age was relatively modest (Figure 4c). The largest changes in biomolecule concentrations over this age sequence were for proteins, which dropped from 3.5% to 0.4% in soils with older radiocarbon ages, and for carbohydrates, which dropped from 3.5% to 0.3% in soils with older radiocarbon ages (Figure 4c). Thus, the BC/OC

![Graph A](https://via.placeholder.com/150)

$R^2 = 0.31$

![Graph B](https://via.placeholder.com/150)

$R^2 = 0.16$

*Figure 3.* (a) The ratio of BC/OC (i.e., the relative abundance of BC) declined with increased precipitation ($n = 44$, $p < 0.05$), such that drier sites had a larger fraction of soil C as BC. (b) The relationship between BC/OC and soil SRO minerals was weak ($n = 44$, $p < 0.05$), suggesting that BC was nearly as responsive to SRO mineral concentrations as was OC.
most likely increases with radiocarbon age because of low inputs of new plant litter to soils (low OC) in the drier sites. Still, we cannot exclude the possibility that the larger relative proportion of BC in the drier sites contributed to older radiocarbon ages in those soils.

4. Discussion

4.1. Controls on BC Preservation

[32] Our data suggest an intriguing pair of hypotheses, which are not mutually exclusive, for understanding drivers of BC retention: mineral adsorption, and direct association with SOC. These controls may have important implications for global BC retention. While BC is one of the few C groups still widely thought to persist in soil because of its inherent chemical recalcitrance [Krull et al., 2006; Marschner et al., 2008], the strong predictive power of SRO minerals for BC concentrations (46% of the variability) observed here suggests that physiochemical stabilization on mineral surfaces may also be important for BC preservation. Several studies have observed the presence of mineral agglomerates or plaques on the surface of soil charcoal particles, as well as BC bound to the surface of soil minerals [e.g., Brodowski et al., 2005; Downie et al., 2011; Glaser et al., 2000; Hockaday et al., 2007], providing some direct evidence for BC interactions with mineral surfaces. The Hawaiian gradient is extreme in its abundance of SRO minerals, but the suggested mechanism may well be a widespread phenomenon, making direct measurement of BC-mineral interactions at the ecosystem scale a priority.

[33] Interestingly, our data also suggest that SOC and BC storage may be directly related. Soil OC can sorb BC (and vice versa) via a variety of mechanisms [Liang et al., 2010; Sohi et al., 2010; Solomon et al., 2007], such that BC is incorporated into SOM-mineral complexes. For example, charged hydrophobic or aromatic SOC components can sorb and flocculate BC via Van der Waals forces (e.g., charge complexation, dipolar, \(\pi-\pi\), etc.) [Pignatello et al., 2006]. Also, BC can sorb dissolved OM onto reactive carboxylic surface groups [Liang et al., 2006], promoting long-term stabilization of C [Glaser et al., 2000, 2001]. The importance of these different mechanisms should be investigated to determine the relative importance of OC relationships versus mineral adsorption for BC stabilization.

[34] We did not find evidence that BC is significantly older than other OC chemical groups, as would be expected if BC were preferentially preserved via inherent chemical recalcitrance. In general, the content of all biomolecules declined with radiocarbon ages in the Hawaiian soils. The positive relationship between BC/OC ratios and soil radiocarbon ages was apparently driven by declines in plant productivity and lower inputs of OC to soils in dry sites, rather than preservation of older BC. However, other studies have found that radiocarbon ages of isolated macroscopic charcoal particles and BC fractions can be older than the bulk SOC [Eckmeier and Wiesenberg, 2009; Krull et al., 2006; Masiello and Druffel, 1998; Pessenda et al., 2001]. Although the method used here captured a broad range of BC morphologies from microscopic soot to macroscopic BC, the BC in our Hawaiian soils was primarily fine grass char, and large unattached particles of BC were nearly

![Figure 4.](image-url)

(a) Radiocarbon ages for bulk soils showed a logarithmic decline in relation to total SOC stocks, with modern radiocarbon signals for C-rich soils, and older signals in C-poor soils \((n = 10, p < 0.05)\). (b) The ratio of BC/OC correlated positively with the radiocarbon age of bulk soils \((n = 10, p < 0.05)\). (c) Cumulative soil C stocks for the six biomolecules relative to soil radiocarbon ages showed declines for all C chemical groups in older soils. The largest declines were in proteins and carbohydrates \((R^2 = 0.67 \text{ and } 0.50, \text{ respectively, } n = 10)\). Proteins declined from 3.5% to 0.4% of soil weight, and carbohydrates declined from 3.5% to 0.3% of soil weight over this time series. Carbonyl, lipids, lignin and BC declined from 1.4%, 1.3%, 0.4%, and 1.7%, to 0.2%, 0.02%, 0.2%, and 0.4%, respectively. Biomolecules listed in the legend are in the same order as graphed from the bottom up, with BC closest to the \(x\) axis.
absent. Thus, it is possible that BC characteristics (e.g., particle size and chemical composition) may provide recalcitrance and promote long-term preservation of BC in other sites [Baldock and Smernik, 2002].

[35] An important component missing from our understanding of BC cycling is BC production and input to ecosystems. Few studies have been able to measure cumulative BC inputs to soils [e.g., Richards et al., 2011]. In this study, woody plant cover was greater at higher fire frequency minimizing the opportunity for subsequent combustion [Czimczik et al., 2005; Glaser and Amelung, 2003]. While we cannot rule out the possibility that differences in cumulative BC inputs across this gradient influenced the trends in BC that we observed, it seems unlikely that inputs would have increased linearly across the gradient along multiple transects. If inputs were driving the observed trends, we would expect much greater variability across the landscape, reflecting wildfire activity and wind patterns. The strong relationships among SRO minerals, OC, and BC observed here suggest that soil mineralogy had a dominant influence on BC retention, masking background variability in inputs.

4.2. Ecosystem Controls on BC at the Global Scale

[36] A number of recent studies have found that landscape- or biome-scale variability in BC abundance is related to ecosystem and soil properties that also drive OC storage, similar to results found here. For example, a global study of 28 mid- to high-latitude grasslands found that BC abundance was highly variable across sites, comprising 5–30% of OC, and yet total OC was strongly related to BC levels [Rodionov et al., 2010], which the authors attributed in part to physical protection via aggregate stability of all C chemical groups. A study of Alaskan boreal spruce forest soils observed BC/OC ratios ranging from 2–27% in mineral soils, and BC abundance was related to a suite of soil properties such as bulk density and soil horizon [Hockaday et al., 2009; Kane et al., 2010]. In a northern steppe, BC accumulation was associated with the silt size fraction in soils, possibly indicated physiochemical adsorption [Rodionov et al., 2006]. Finally, a study in Siberian tundra found that landscape-scale variability in permafrost and active layer depths affected BC and OC storage similarly [Guggenberger et al., 2008]. These studies all suggest that soil properties and processes that drive OC storage also affect BC storage. In contrast, an Australian study found BC and OC to be essentially uncorrelated across sites with different soil type, vegetation, management, fire regime and climate [Janik et al., 2007]. The lack of correlation in the Australian study could result from the large number of differing factors among the sites, indicating that relationships between OC and BC storage may not hold across biome and management gradients. Nonetheless, it is clear that soil properties that control OC storage can play a large role in driving BC retention and pool sizes worldwide. This Hawaiian gradient provides strong indication that soil mineralogy in particular has the potential to drive BC storage in ecosystems.

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