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Variability in oxidative degradation of charcoal: influence of production conditions and environmental exposure.

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Abstract

Charcoal is a key component of the Black Carbon (BC) continuum, where BC is characterized as a recalcitrant, fire-derived, polyaromatic material. Charcoal is an important source of palaeoenvironmental data, and of great interest as a potential carbon sink, due to its high apparent environmental stability. However, at least some forms of charcoal are clearly susceptible to environmental alteration and degradation over relatively short timescales. Although these processes have importance for the role of charcoal in global biogeochemistry, they remain poorly understood.

Here we present results of an investigation into the susceptibility of a range of charcoal samples to oxidative degradation in acidified potassium dichromate. The study examines both freshly produced charcoal, and charcoal exposed to environmental conditions for up to 50,000 years. We compare the proportion of carbon present in different forms between the samples, specifically with respect to the relative chemical resistance of these forms. This was undertaken in order to improve understanding of the post-depositional diagenetic changes affecting charcoal within environmental deposits.

A wide range in chemical compositions are apparent both within and between the sample groups. In freshly produced charcoal, material produced at 300°C contains carbon with more labile forms than charcoal produced at $\geq 400^\circ\text{C}$, signifying a key chemical change over the 300-400°C temperature range. Charcoal exposed to environmental depositional conditions is frequently composed of a highly carboxylated aromatic structure and contains a range of carbon fractions of varying oxidative resistance. These findings suggest that a significant number of the environmental charcoals have undergone post-depositional diagenetic alteration. Further, the data highlight the potential for the use of controlled progressive oxidative

degradation as a method to characterize chemical differences between individual charcoal samples.

Keywords

Charcoal, Oxidative degradation, Black carbon, Biochar

1 INTRODUCTION

A key component of global carbon cycles is “Black Carbon” (BC), the fire-derived product of biomass, with an estimated 40-270 Tg year⁻¹ of BC produced via global biomass burning (Kuhlbusch et al., 1996). Black Carbon is frequently characterized by high aromaticity, high oxidative resistance and a demonstrably pyrogenic origin (Bird and Gröcke, 1997; Schmidt and Noack, 2000; Preston and Schmidt, 2006; Scott, 2010) and the term ‘BC’ is applied to a broad continuum of materials, including char, charcoal and soot (Goldberg, 1985; Seiler and Crutzen, 1980; Hedges et al., 2000; Schmidt et al., 2001; Maisello, 2004; Scott, 2010).

BC is chemically highly stable and environmentally recalcitrant, due to a polyaromatic structure (Simpson and Hatcher, 2004, Haumeier and Zech, 1995), and is one of the most slowly cycling components of terrestrial and marine carbon reservoirs (Masiello and Druffel, 1998; Schmidt et al., 2002). The ~5-7ky half-life of BC-containing materials in soils (Preston and Schmidt, 2006), greatly exceeds the mean residence time of bulk organic carbon in surface soil and subsoil (~300 years and ~2500 years respectively (Fontaine et al., 2007)). Therefore, there is considerable interest in the potential of BC as a major atmospheric carbon sink (Lal, 2008; Lehmann et al., 2006). However, it is also clear from recent research that various forms of BC may be subject to environmental alteration and degradation on shorter timescales (Schmidt and Noack, 2000; Bird et al., 1999; 2002; Kaal et al., 2007; Ascough et al., 2010a; 2010b; 2011). Both biotic and abiotic mechanisms are proposed for the alteration of BC in soils. For example, BC surfaces can provide a microhabitat for soil microbes (Wardle et al., 1998; Pietikäinen et al., 2000; Hockaday

et al., 2007; Ascough et al., 2010c), and BC mineralization is observed during laboratory incubations (Baldock and Smernik, 2002; Hamer et al., 2004).

Clear variations exist in production mechanism, chemical properties and environmental dispersal between BC materials (Gelinas *et al.*, 2001). A significant component of the BC continuum is charcoal, the solid product of biomass exposed to elevated temperatures in restricted oxygen availability (Antal and Grønli, 2003; Scott, 2010). During charcoal production lignocellulosic fragments are thermally degraded and undergo large-scale rearrangement into aromatic structures (Antal and Grønli, 2003). As higher charring temperatures are reached (e.g. >700°C), highly ordered, 'graphitic' polyaromatic microcrystalline domains become evident within charcoal microstructure (Darmstadt et al., 2000; Cohen-Ofri et al., 2006). Some charcoal carbon is therefore a highly recalcitrant, polyaromatic substance, surviving in near-pristine condition and identifiable to species level even after millennia of environmental exposure (e.g. Scott, 2000; 2010).

Despite this, charcoal is clearly not a homogeneous substance, and forms a continuum of compositional types dependent upon production variables, especially temperature. This produces chemical structures in charcoal that range from material similar to uncharred biomass, to material with features of completely ordered graphite. For example some lower-temperature (i.e 300°C) material may retain incompletely degraded lignocellulosic fragments (Ascough et al., 2008). Physical and chemical properties of charcoal therefore vary widely, and charcoal is a heterogeneous substance composed of thermally altered biomacromolecules (Baldock and Smernik, 2002; Knicker, 2007; Knicker et al., 2008). Some charcoal also clearly undergoes environmental alteration and degradation, as charcoal carbon is progressively lost from cave deposits as well as savannah and boreal soils (Harden *et*

al., 2000; Bird *et al.*, 1999 Bird *et al.*, 2002), and substances chemically consistent with charcoal degradation products are present in soils and sediments (Haumeier and Zech., 1995; Hockaday *et al.*, 2007).

Oxidative processes, particularly carboxylation, appear to be important in charcoal alteration processes (Cohen-Ofri *et al* 2006), suggesting that charcoal more susceptible to oxidative attack is more likely to undergo alteration in the environment. However, the factors influencing such susceptibility in charcoal are not well understood. The degree of post-depositional diagenetic alteration does not necessarily correlate with the time period of environmental exposure (Cheng *et al.*, 2008; Liang *et al.*, 2008), suggesting that charcoal production variables and chemistry of the depositional environment are more likely to control charcoal alteration. Ambiguity also surrounds the provenancing of different carbon fractions within charcoal recovered from environmental deposits; are these production-derived, or do they represent the effects of post-depositional diagenesis? This uncertainty means that confidently identifying diagenetically altered charcoal can be difficult.

BC quantification is frequently operationally defined, where the specific criteria for definition depend upon the particular methodological approach (Hammes *et al.*, 2007). An approach that allows identification of the presence and oxidative resistance of different fractions within carbonized biomass is oxidation with acidified potassium dichromate ($K_2Cr_2O_7$) (e.g. Wolbach and Anders 1989; Bird and Groke, 1997). This is commonly used to quantify the BC component in environmental matrices, when the aim is to maximize both removal of labile material and recovery of the BC fraction and oxidation is performed for a single time interval. However, where sufficient sample is available, it is also possible to use the $K_2Cr_2O_7$ method to compare the various proportions and reactivity of different sample fractions, via the construction of

oxidation rate curves (e.g. Wolbach and Anders, 1988; Bird and Gröcke, 1997; Masiello *et al.*, 2002). Here we use this approach to contrast the proportion and nature of carbonaceous fractions within different charcoal types. This includes both material freshly-produced under a range of pyrolysis conditions (including open fires), and charcoal exposed to environmental conditions for time intervals of up to 50,000 years. The results are discussed with respect to the post-depositional alteration of charcoal, and the implications of this alteration for understanding of the role of charcoal in the environment.

2 MATERIALS AND METHODS

2.1 Charcoal samples

Freshly-produced charcoal was prepared in laboratory-controlled conditions and on open fires (Fr_{char}), while charcoal exposed to environmental conditions (Env_{char}) was recovered from archaeological and sedimentary deposits (Table 1).

For laboratory-produced Fr_{char} , 1cm^3 cubes of either Scots pine (*Pinus sylvestris*) or mangrove (*Rhizophora apiculata*) wood were converted to charcoal in a rotary tube furnace at four temperatures (300, 400, 500 and 600°C). Once the required temperature was reached, the sample was heated for 60 minutes under either inert (100% N_2) conditions, or in the presence of 2% O_2 (see Ascough et al., 2008). Two charcoal samples were also produced from *Pinus sylvestris* cubes on an open fire for an equivalent time to the laboratory-produced charcoal. Oxygen availability was restricted during production of these samples by wrapping the wood in aluminium foil during heating. A sample of commercially produced Highly Ordered Pyrolytic Graphite (HOPG, SPI supplies) was also obtained. This was included in the suite of Fr_{char} to represent an ordered polyaromatic structure comprised of 100% graphitic carbon.

13 samples of Env_{char} (Env-1 to Env-13) were obtained from archaeological and natural deposits. The age of the samples are based upon radiocarbon (^{14}C), or stratigraphic grounds, and range from <50 years (129.7 ± 0.4 pMC) to 50,000 years. Material was obtained from previously excavated archaeological sites over an environmental range from high-latitude boreal to low-latitude tropical zones (see Table 1) via liaison with the site excavators. All Env_{char} was isolated from the sedimentary matrix by conventional water floatation, which removed visible soil

contaminants. Samples were inspected in the lab and further soil material was removed by sonication in deionized (Milli-Q™) water in the lab for 2 hours, followed by air-drying at 40°C.

Fr_{char} and Env_{char} were lightly crushed and the 63-500 µm fraction isolated by sieving. Calcitic ash and soil carbonates were removed by a 0.5M HCl wash, after which charcoal was rinsed three times in Milli-Q™ water and air-dried at 40°C. Mineral ash contents were determined by loss on ignition at 1020°C, where measurement precision based on three replicates was ± 0.5%. Fr_{char} ash contents were generally <1%, however ash contents were higher in some Env_{char}. Elemental abundance values were consequently calculated on an ash-free basis.

2.2 Chemical oxidation

Dichromate oxidations followed the method of Bird and Gröcke, (1997), using between 0.1 and 0.15g of dry charcoal. The initial weight was selected to ensure sufficient sample remained for analysis following oxidation. The charcoal was mixed with 40ml of 0.1M K₂Cr₂O₇ in 2M H₂SO₄ in a capped centrifuge tube and placed in a controlled temperature incubator shaker. Oxidations took place at 60°C for time periods of up to 4136 hours (i.e. 172 days). The K₂Cr₂O₇ was sometimes exhausted before the end of the oxidation period. This was identifiable by discolouration of the orange solution, which was then removed by centrifugation and decanting, and fresh reagent added. After the pre-determined oxidation period, solid charcoal was separated from solution by centrifugation and filtration. Samples were then washed three times in Milli-Q™ water to remove remaining K₂Cr₂O₇.

Samples were transferred to clean glass vials by pipette in Milli-QTM water and frozen. Oxidative mass losses were then determined following lyophilization. Care was taken at each step to minimize sample losses. Uncertainties due to recovery were $\pm 3\%$ by weight, based on replicate measurements of a 300°C pine charcoal following identical treatment using Milli-QTM water in place of K₂Cr₂O₇ solution.

2.3 Elemental and isotopic analysis

Carbon content (%C) and isotopic values ($\delta^{13}\text{C}$) were determined for samples prior to and following K₂Cr₂O₇ oxidation. Measurements were made on a Costech elemental analyser (EA) (Milan, Italy) fitted with a zero-blank auto-sampler. The EA was linked via a ConFloIII to a ThermoFinnigan Delta^{plus} XL isotope ratio mass spectrometer (Thermo Finnigan GmbH, Bremen, FRG) as described in Werner et al., (1999). Samples were measured in duplicate, along with a mix of blanks and laboratory standards. The standards were acetanilide (IAEA/Sigma Aldrich; %C: 71.09%, $\delta^{13}\text{C}$: -30.11‰), a commercially available protein (Organic Analytical Standard B2155, Elemental Microanalysis; %C: 47.02, $\delta^{13}\text{C}$: -26.98‰) and a C₄ cane sugar/uric acid mix (Tesco; %C: 40.20, $\delta^{13}\text{C}$: -12.02‰). External reproducibility for %C was better than 0.5%. Isotopic values are reported as per mil (‰) deviations from the VPDB international standard. The measurement precision was better than $\pm 0.3\%$ (1 σ) for %C, and $\pm 0.2\%$ (1 σ) for $\delta^{13}\text{C}$.

Oxygen content (%O) of samples was obtained prior to K₂Cr₂O₇ oxidation, and at selected points during K₂Cr₂O₇ treatment to determine the net effect of oxidation on sample %O. Measurements were made using a Thermo Finnigan high temperature conversion elemental analyser (TC/EA) linked to a Thermo Delta^{Plus}

Advantage isotope ratio mass spectrometer (both Thermo Finnigan GmbH, Bremen, FRG), with acetanilide (IAEA/Sigma Aldrich, %O: 11.84%) as the internal standard. External reproducibility for %O was better than 0.7%.

2.4 FTIR

Fourier Transform Infrared Spectroscopy (FTIR) using the mid-infrared region of the electromagnetic spectrum ($\sim 4000\text{--}400\text{ cm}^{-1}$) reveals qualitative detail regarding the nature of chemical bonds in biomass, including charcoal (e.g. Moore and Owen, 2001; Nishimiya et al., 1998; Guo and Bustin, 1998). Selected samples were subjected to FTIR prior to $\text{K}_2\text{Cr}_2\text{O}_7$ oxidation, and following progressive oxidation. This allowed a comparison of the chemical forms present within individual charcoal samples that displayed different rates of degradation during chemical oxidation.

Dry samples were diluted by grinding with solid KBr and pressed into pellets. Analyses were performed using a Nicolet FTIR with absorbance values determined between 4000 and 400 cm^{-1} . Spectral bands were subsequently identified by comparison with published assignments (Table 2). The Fr_{char} and Env_{char} samples analysed were chosen to represent different end members with respect to resistance to $\text{K}_2\text{Cr}_2\text{O}_7$ oxidation, including the most and least resistant charcoals of both sample sets. The Fr_{char} included charcoal produced at the lowest (300°C) and highest (600°C) temperatures, under both N_2 and 2% O_2 , and the Env_{char} included Env-1, Env-2, Env-5, Env-6, Env-10, and Env-13. FTIR spectra for unoxidized Fr_{char} produced under N_2 at 300°C and 600°C , and for Env-1, Env-2, Env-5, and Env-6, are previously reported in Ascough et al (2011).

2.5 ^{13}C -CPMAS NMR spectroscopy

Solid-state ^{13}C Nuclear Magnetic Resonance Spectroscopy, using cross-polarization magic angle spinning (^{13}C -CPMAS NMR spectroscopy) is used to reveal detail in the chemical structure of specific carbon (C) environments within carbonized biomass based upon the ^{13}C signal intensity and chemical shift (e.g. Baldock and Smernik, 2002; Simpson and Hatcher 2004). Selected samples were subjected to ^{13}C -CPMAS NMR spectroscopy, including Fr_{char} produced at the lowest (300°C) and highest (600°C) temperatures under N_2 and Env_{char} sample Env-1. These were chosen to represent charcoal end members with high and low chemical oxidative resistance. ^{13}C -CPMAS NMR spectra were recorded on a 400 MHz Varian VNMRS instrument operating at 100.56 MHz for ^{13}C and using a 4mm magic-angle spinning probe with a zirconium oxide rotor fitted with Teflon end caps. Spectra were referenced to external, neat tetramethylsilane, and for cross polarization typical acquisition conditions were a 1 s recycle delay, 1 ms contact time and a sample spin-rate of 12 kHz. A variable (ramped) amplitude 1H spin-lock pulse was used for the cross polarization step. The pulse sequence incorporated a spin-echo to suppress a broad background signal from the Vespel spinner housing; this has resulted in a small amount of signal arising from the Teflon rotor caps being observed in some spectra at ~111 ppm.

RESULTS

2.6 Oxidative carbon loss rates

Large differences were observed during $K_2Cr_2O_7$ oxidation between Fr_{char} prepared at $300^\circ C$ and Fr_{char} prepared at $\geq 400^\circ C$ (Table 3). The $\geq 400^\circ C$ Fr_{char} consists of a single resistant carbon component, with an oxidative half life ($T_{1/2}$) on the order of 800-1000 hours, similar to that of the HOPG. Overall oxidative resistance of Fr_{char} is directly correlated with production temperature, and is higher in samples prepared in 2% O_2 . Mangrove charcoal also appears more resistant than pine charcoal prepared under identical conditions. Fr_{char} produced in open fires shows similar oxidative resistance to the $\geq 400^\circ C$ Fr_{char} (e.g. <20% C loss after >200 hours oxidation).

In the $300^\circ C$ Fr_{char} at least two carbon components of different oxidative resistance are visible, identifiable by a change in the rate of oxidative C loss. Both of these have lower oxidative resistance than the $\geq 400^\circ C$ Fr_{char} and even the most resistant carbon in these samples has $T_{1/2}$ on the order of <100 hours. In $300^\circ C$ Fr_{char} produced under N_2 , pine charcoal is more labile than mangrove charcoal during $K_2Cr_2O_7$, for example 80% of C in sample P-300 is removed in <1 hour of oxidation. However in $300^\circ C$ Fr_{char} produced under 2% O_2 , mangrove charcoal is more labile, although C loss still approaches completion after 432 hours of oxidation.

Differences in %C loss rates are apparent between the Env_{char} samples during $K_2Cr_2O_7$ oxidation. (Table 4). A highly resistant component, (with $T_{1/2}$ of 300-1500 hours) is visible in all Env_{char} with the exception of Env-2. Samples Env-1 and Env-9 appear to consist solely of this material; only <40% of sample C is removed from Env-1 in >4000 hours of oxidation. In other Env_{char} the amount of the highly resistant carbon typically comprises 20-40% of total sample C, but varies between samples.

As well as a highly resistant component, the majority of Env_{char} contains at least two other C components of lower oxidative resistance. The most labile of these is removed in <24 hours $\text{K}_2\text{Cr}_2\text{O}_7$ oxidation. This is apparent in Env-5, where 61% of sample C is oxidized with $T_{1/2}$ of 2 hours and in Env-2, where 80% of sample C is removed in 4 hours. A second component has intermediate oxidative resistance, with $T_{1/2}$ of 30-100 hours, and is responsible for the majority of sample C removal up to ~250 hours oxidation.

2.7 $\delta^{13}\text{C}$ variation with oxidative C loss

Values of $\delta^{13}\text{C}$ for Fr_{char} prior to $\text{K}_2\text{Cr}_2\text{O}_7$ oxidation are reported in Ascough et al., (2008). Following progressive $\text{K}_2\text{Cr}_2\text{O}_7$ oxidation, $\delta^{13}\text{C}$ changes are largest in the 300°C Fr_{char} samples (Table 3). Note that in M-300, extensive removal of sample C during oxidation (>99%) precluded reliable measurement of $\delta^{13}\text{C}$. In 300°C Fr_{char} prepared under N_2 , the $\delta^{13}\text{C}$ fluctuates by up to +1.2‰ during oxidation. This indicates progressive removal of isotopically distinct components. In 300°C Fr_{char} prepared under 2% O_2 , significant changes in $\delta^{13}\text{C}$ only occur after >100 hours of oxidation. For Fr_{char} produced at $\geq 400^\circ\text{C}$, and in open fires, only small ^{13}C variations occur after even ~800 hours oxidation; these changes are not correlated with wood species or production variables. In the 600°C pine and mangrove Fr_{char} , $\delta^{13}\text{C}$ changes are only observed after >1000 hours oxidation. These are +0.3‰ in pine charcoal and +4.0‰ in mangrove charcoal.

Values of $\delta^{13}\text{C}$ for untreated Env_{Char} samples Env-7, Env-8 and Env-9 are reported in Ascough et al., (2011). No significant change in $\delta^{13}\text{C}$ occurs during oxidation up to 1000 hours of Env-1, Env-9, Env-11 and Env-13 (Table 4). The

remaining 9 Env_{Char} samples show some change in $\delta^{13}\text{C}$, mainly after 24 hours oxidation. However even after removal of a large proportion of sample C, the changes in Env_{Char} $\delta^{13}\text{C}$ variations are <1‰ relative to the unoxidized charcoal. A larger $\delta^{13}\text{C}$ change (of up to -2.5‰) is only observed after ~300 hours oxidation in Env-12.

2.8 O/C ratio variation with oxidative C loss

Atomic O/C ratios of charcoal can vary with starting material (e.g. grass char versus wood char (Hammes et al., 2006)), however in wood charcoal, O/C ratios show an overall linear correlation with production temperature (Ascough et al., 2010a). By comparison with the O/C ratio of Fr_{char} produced at known temperatures, the O/C ratio of Fr_{char} produced on open fires (0.11) suggests production at >500°C. All Env_{char} except Env-1 have O/C ratios between 0.55-0.34, notionally equivalent to Fr_{char} produced at ~250-400°C.

Oxidative addition of oxygen atoms increases the O/C ratios of Fr_{char} on the order of <0.15 (Table 3). O/C increases are slight in Fr_{char} produced at 300°C, even after the loss of up to 80% sample carbon. O/C increases are larger in $\geq 400^\circ\text{C}$ Fr_{char} particularly after periods of >500 hours oxidation. These increases are larger in pine charcoal than in mangrove charcoal. O/C increases of up to 0.4 are observed in 600°C Fr_{char} after oxidation of >4000 hours.

Values of %O for Env-1, Env-2, Env-5, Env-6, and Env-13 prior to dichromate oxidation are reported in Ascough *et al* (2010b). In the oxidized Env_{char}, slight increases in O/C ratio are observed, but even after >1000 hours of oxidation these are smaller than in the Fr_{char} (Table 4). For example, in Env-1 after >4000 hours oxidation

O/C increases by only 0.2. The exception is Env-2, where an O/C increase of 0.23 is observed after 5 hours oxidation.

2.9 FTIR

Fourier Transform Infrared spectra of 300°C versus 600°C Fr_{Char} produced under N₂ are significantly different (Ascough *et al.*, 2011). The 600°C Fr_{Char} spectra are dominated by aromatic C=C (1590-1560 cm⁻¹), and aromatic C-H out-of-plane deformation (700-900 cm⁻¹). However 300°C Fr_{Char} also contains aliphatic CH_x (1450 cm⁻¹), oxygenated functional groups of cellulose (1030-1160 cm⁻¹), lignin (1510 cm⁻¹), carboxylic (COOH) and carboxylate (COO⁻) groups (~1715 cm⁻¹ and ~1605 cm⁻¹, respectively).

The FTIR spectra of Fr_{Char} produced at 600°C under 2% O₂ are not significantly different to those of samples produced under N₂ (Figure 1A). This is also true for mangrove 300°C Fr_{Char} produced under 2% O₂. However pine Fr_{Char} produced at 300°C under 2% O₂ shows large attenuation of signal for lignocellulosic material, compared to equivalent sample produced under N₂ (Figures 1A and 1B). This has been attributed to more efficient carbonization of pine charcoal in the presence of oxygen, which results in a more highly aromatic charcoal structure (Ascough *et al.*, 2008).

Oxidation by K₂Cr₂O₇ does not produce major spectral alteration in mangrove 300°C Fr_{Char} or pine 300°C Fr_{Char} produced under 2% O₂ (Figures 1A and 1B). In pine 300°C Fr_{Char} produced under N₂ the intensity of lignocellulosic peaks is reduced, and intensity of the carboxylic/carboxylate peaks (~1600 cm⁻¹ and ~1700 cm⁻¹) is increased following 24 hours K₂Cr₂O₇ oxidation. Extended oxidation of 600°C

Fr_{char} up to 1008 hours results in development of a strong peak at $\sim 1710\text{ cm}^{-1}$, indicating oxidation of C=C structures to form COOH groups.

The Env_{Char} samples are composed overall of highly carboxylated, dominantly aromatic structures, with a cellulosic component in Env-5 (Ascough *et al.*, 2011). The exception is Env-1, which is dominantly aromatic with a minor COOH contribution ($\sim 1700\text{ cm}^{-1}$) (Ascough *et al.*, 2011).

Cellulosic signal is removed from Env-5 after 72 hours K₂Cr₂O₇ oxidation, and in Env-2 the appearance and subsequent removal of bands at 833, 852 and 884 cm^{-1} indicates degradation of conjugated aromatic structures (Figure 1C). However in other samples spectral changes only occur after extensive oxidative loss of sample carbon. In the spectra of Env_{Char} following extensive carbon loss (i.e. after extended oxidation), signal from mineral components becomes prominent in several samples, particularly quartz (1080 cm^{-1}). In Env-1 COOH signal increases markedly at 1713 cm^{-1} after 4176 hours K₂Cr₂O₇ oxidation, signifying oxidation of the condensed aromatic structure (Figure 2C).

2.10 ¹³C-CPMAS NMR spectroscopy

¹³C-CPMAS NMR spectra of 300 °C pine and mangrove Fr_{char} contain peaks at 60-105 ppm from cellulosic carbons, and at 55 ppm from lignin methoxy groups (Figures 2A and 2B). These spectra also contain a range of signals centred at ~ 130 ppm and attributed to condensed aromatic structures. Progressive K₂Cr₂O₇ oxidation does not result in major spectral alteration, although in pine 300°C Fr_{char} there is a loss of intensity relating to cellulosic carbons. Signal remains in these samples from lignin monomers (55 and 146 ppm), plus aliphatic -CH₂ and -CH₃ structures (15-30 ppm).

The dominantly aromatic ^{13}C -CPMAS NMR spectra from Fr_{char} produced at 600°C under N_2 is not significantly altered by 1000 hours of oxidation. The slight change to higher frequency of the shift of the aromatic band, and lower overall signal-to noise ratio in the spectrum, are both consistent with the loss of C-H carbons. ^{13}C -CPMAS NMR spectra of Env-1 comprises a single aromatic signal centred on ~ 125 ppm (Figure 2C), with high and low frequency spinning sidebands (*), characteristic of charcoal produced $>500^\circ\text{C}$ (Ascough et al., 2008). After 4136 hours of oxidation, there is a suggestion of low-intensity signals developing around 170 ppm and 190 ppm; it is possible these could indicate formation of carboxylic and ketone groups, respectively.

3 DISCUSSION

Fr_{char} and Env_{char} samples show large variation in resistance to $K_2Cr_2O_7$ oxidation, highlighting important chemical differences between charcoal samples. During production of Fr_{char} key chemical changes occur around $400^\circ C$. At this point cellulosic material is largely removed, and aromatic condensation is the dominant process (Eckmeier *et al.*, 2007). Consequently, Fr_{char} produced at $\geq 400^\circ C$ appears homogeneous, largely aromatic and recalcitrant relative to the $300^\circ C$ Fr_{char} . Fr_{char} produced at $400-600^\circ C$ requires $K_2Cr_2O_7$ oxidation on the order of several hundred hours before significant degradation (see also Knicker *et al.*, 2007b). Oxidative degradation of $\geq 400^\circ C$ Fr_{char} involves carboxylation of the aromatic structure. In $\geq 400^\circ C$ Fr_{char} the increases in $\delta^{13}C$ following oxidation can be attributed to the preferential loss of ^{12}C during break-up of aromatic units. This process, rather than the preferential loss of isotopically different compounds, is more likely to affect oxidative $\delta^{13}C$ changes in $\geq 400^\circ C$ Fr_{char} as these samples are relatively homogeneous. However, it is also important to note that charcoal produced from different plant biopolymers (e.g. cellulose and lignin) exhibits different stabilities during $K_2Cr_2O_7$ oxidation (Knicker, 2010). The relative proportions of carbons from different plant biopolymers in different charcoal samples can also vary depending on the starting material (Ascough *et al.*, 2008). These factors could therefore influence the rate of $\delta^{13}C$ change during oxidation between different $\geq 400^\circ C$ Fr_{char} samples.

The aromatic fraction within Fr_{char} produced at $300^\circ C$ oxidises more rapidly than in the $400-600^\circ C$ Fr_{char} , suggesting the domain size of polyaromatic units is smaller overall in the $300^\circ C$ Fr_{char} . In organized carbon structures oxidative C loss is more energetically favourable at sites of irregularities such as edge sites. Oxidative C loss is therefore more rapid in materials with smaller polyaromatic domains, as many

edge sites are exposed in these substances (Walker et al., 1959; Boehm et al., 1994). This may explain the close correspondence between initial charcoal O/C ratios and subsequent dichromate oxidation rates, as aromatic structures with a larger number of edge and defect sites are likely to contain a higher proportion of O atoms.

Fr_{char} produced at 300°C is considerably more heterogeneous than Fr_{char} produced at $\geq 400^\circ\text{C}$, containing several isotopically distinct C fractions. These appear to be composed of both thermally-altered, dominantly aromatic material, and plant biopolymers that have undergone incomplete thermal conversion. The different C fractions have different resistance to chemical oxidation, with the most labile being the incompletely converted lignocellulosic structures. This effect was also noted by Knicker, (2010). Some signal attributable to lignocellulosic carbons is visible in the FTIR and ^{13}C -CPMAS NMR spectra of 300°C Fr_{char} after 24 hours of oxidation (Figures 2 and 3). Although this signal is drastically attenuated versus the unoxidized samples, it indicates at least some non-aromatic carbons in charcoal can resist $\text{K}_2\text{Cr}_2\text{O}_7$ treatment for this time. However, it is also important to note the potential for over-representation of lignocellulosic carbons in ^{13}C -CPMAS NMR spectra of material such as charcoal, due to the slower cross polarization rates of carbons in polyaromatic structures (i.e. those remote from protons) versus carbons in structures such as cellulose, which are directly attached to protons (Alemany *et al.*, 1983). Similar survival of alkyl-C and lignocellulosic material during chemical oxidation has been observed for soil and plant BC samples, resulting from chemical or physical protection within the sample matrix, including hydrophobic effects (Knicker *et al.*, 2007b). This highlights the potential for over-estimation of sample BC content when using the dichromate oxidation method (Wolbach and Anders, 1989; Bird and Gröcke, 1997) for BC quantification (Knicker *et al.*, 2007b). Therefore if these effects are

considered likely, chemical characterization of sample residues following $K_2Cr_2O_7$ oxidation may be desirable, to ensure that the isolated material is endogenous. This is a consideration in BC quantification studies, but also in interpretation of fire histories, as BC concentrations estimated by chemical methods can differ from charcoal estimates made using microscopic methods.

The majority of Env_{char} samples are markedly different from the Fr_{char} , particularly Fr_{char} produced at $\geq 400^\circ C$ and on open fires, containing at least three main carbon fractions of different oxidative resistance. The proportions of these vary widely between samples, however isotopic differences between carbon fractions isolated during oxidation and the unoxidized charcoal are usually $<1-2\%$. This is comparable to that expected within an individual plant (Leavitt and Long, 1984; McCarroll and Loader, 2004; Wilson and Grinstead, 1977), suggesting the majority of C in the Env_{char} samples is endogenous.

In most Env_{char} , $\sim 10\%$ of C is highly aromatic and resistant; this is the fraction apparent in the %C loss rate curves after ~ 300 hours as the rate of oxidative C loss reaches a minimum. The oxidation rate of this material is similar to that of C within Fr_{char} produced at $\geq 400^\circ C$, Fr_{char} produced in natural fires, and HOPG. However only Env-1 is dominantly composed of this resistant C, and in other Env_{char} samples, two further carbon fractions are visible, in contrast to the Fr_{char} samples. Approximately half the Env_{char} samples contain a C component that is labile in the initial oxidation stages, typically resulting in loss of 20-30% of sample C, but reaching $\sim 60\%$ C loss in Env-5 and $\sim 80\%$ C loss in Env-2. This is surprisingly high, given that all unoxidized Env_{char} on visual inspection consisted of fully charred material with no evidence of structural degradation. Overall this component appears dominantly aromatic, although a small proportion of lignocellulosic material is

apparent in some samples (e.g. Env-5). Again, FTIR spectra show incomplete removal of non-aromatic components in some samples after 5 hours oxidation (Figure 3C).

Secondly, an Env_{char} C component of intermediate resistance is removed within ~300 hours $\text{K}_2\text{Cr}_2\text{O}_7$ oxidation. The major changes in Env_{char} during $\text{K}_2\text{Cr}_2\text{O}_7$ oxidation relate to the degradation of aromatic structures, rather than the removal of distinctly different chemical compounds. Sample loss at ~24-300 hours oxidation therefore appears to result from removal of aromatic structures that are more “degradable” than those remaining after 300 hours oxidation, implying a proportionally smaller size of aromatic domains in more labile components than in the more resistant fraction.

$\text{K}_2\text{Cr}_2\text{O}_7$ oxidation of the Env_{char} suggests that production temperatures were below 400°C in at least some samples, particularly those containing lignocellulosic structures that have undergone incomplete thermal conversion. Mean random reflectance (Ro_{mean}) gives charcoal production temperatures of $320 \pm 29^\circ\text{C}$ to $361 \pm 25^\circ\text{C}$ for Env-2, Env-3, Env-4, and Env-5 (Ascough *et al.*, 2010a). It is therefore likely that a proportion of the least resistant C fraction (i.e removed in <24 hours oxidation) in Env_{char} represents a heterogeneous mixture of small aromatic structures and the remains of original plant material that had undergone incomplete thermal conversion during pyrolysis. An implication of these results is that such material is likely to be preferentially lost during $\text{K}_2\text{Cr}_2\text{O}_7$ oxidation of samples containing mixed charcoal with a range of aromatic domain sizes.

If Env_{char} samples were produced at $\geq 400^\circ\text{C}$, the results of chemical oxidation suggest that alteration has occurred in the environment, and rendered a portion of (originally) highly resistant carbon more susceptible to oxidation by $\text{K}_2\text{Cr}_2\text{O}_7$. In Env-1 and Env-6 Ro-based production temperatures are $516 \pm 33^\circ\text{C}$ and $497 \pm 25^\circ\text{C}$,

respectively (Ascough *et al.*, 2010a). In Env-1 the pattern of slow, uniform, oxidative carbon loss is consistent with production at 500°C. However in Env-6 a range of carbon fractions are visible, leading to changes in C loss rates during progressive oxidation, inconsistent with the Ro-based production temperature. Carboxylation has been identified as a key process indicative of environmental diagenetic alteration in charcoal (Cohen-Ofri *et al.*, 2006; Kaal *et al.*, 2007), and it is notable that all except one of the Env_{char} samples contain prominent carboxylic and carboxylate groups. The exception (Env-1) comprises a homogeneous highly aromatic structure that oxidizes extremely slowly, suggestive of a pristine, unaltered charcoal originally produced at $\geq 400^\circ\text{C}$.

The results indicate wide variability in both the initial post-production chemical structure of charcoal, and in the effects of exposure to environmental conditions. The former are intimately linked to production variables, particularly temperature and starting species, and potentially dictate the susceptibility of charcoal to environmental alteration. It is also likely that the specific depositional environment influences the nature and intensity of diagenetic alteration. For example, the presence of mineral oxides within the soils during deposition may catalyse the degradation of the charcoal structure, by lowering the activation energy required for oxidative reactions (Elmqvist *et al.*, 2004). The redox potential and pH of the depositional environment is also likely to determine the rate of diagenetic processes. Chabbi *et al.*, (2006) found that mineralization of recalcitrant organic carbon from lignite increased at higher redox potentials, while Braadbaart *et al.*, (2009) found greater physical and chemical degradation of charcoal at higher pH. Biotic processes may also alter charcoal chemistry in the environment, via microbial mediation of degradation, the potential of which is highlighted in both laboratory incubations and within native soil (Shneour,

1966; Shindo, 1991; Petsch et al., 2001; Baldock and Smernik, 2002; Hamer et al., 2004; Ascough et al., 2010c). However, much further work is clearly required to understand the complex interplay between depositional environments and abiotic or biotic alteration of charcoal within the environment.

The interaction between production conditions and deposition environment considerably complicate the interpretation of chemical analyses on charcoal samples. A useful methodological approach in this regard may involve quantification of production temperature, using such techniques as mean random reflectance (Ro) or BCPA (e.g. Glaser et al., 1998; Scott and Glasspool, 2005). Where these techniques indicate production at temperatures $>400^{\circ}\text{C}$ in charcoal samples that oxidize rapidly in $\text{K}_2\text{Cr}_2\text{O}_7$ and contain COOH groups, this may indicate post-depositional alteration of the aromatic structure.

The possibility that the aromatic structure of charcoal may be mineralized during environmental deposition has important implications for models of carbon cycling. In order for such models to be accurate, it is important that the post-depositional fate of charcoal carbon is adequately understood and accounted for. In addition, the presence of a substantial proportion of original sample carbon in ancient charcoals that exists in forms other than that traditionally defined as BC has important implications for environmental studies. The material is more labile and hence likely to be more rapidly mineralized than the BC fraction, meaning it may be overlooked in quantification studies. Future quantitative investigation of the global inventory of carbon stored as BC within the soil should therefore not only seek to isolate the most condensed and recalcitrant fraction of charcoal carbon, but should also include assessments of BC forms that may have been subject to alteration and degradation. In soils containing charcoal, examples of these include the alkali-soluble, highly carboxylated, aromatic

substances that are operationally defined as 'humic acids'. Several studies have shown that some forms of humic acid are attributable to the alteration products of charred biomass (Kumada, 1983; Shindo et al., 1986a; Shindo et al., 1986b; Haumeier and Zech, 1995; Ascough et al., 2011). Such processes appear more likely in areas with high oxidation rates within soils subjected to frequent fire incidence and the formation of 'pyromorphic humus' (González-Pérez et al., 2004). In summary, the results of this study emphasises that charcoal itself forms a continuum of carbonaceous fractions (see also Knicker et al., 2008), and may exhibit widely different behaviour and susceptibility to alteration during environmental deposition.

4 CONCLUSIONS

Extended oxidation studies of charcoal samples reveal important differences between samples. These consist of differences in the chemical form in which carbon is hosted within charcoal, particularly with respect to oxidative resistance. The proportions of these different C fractions present vary considerably between charcoal samples and appear predominantly dependent upon i.) Production temperature, and ii.) Alteration during exposure to environmental conditions. In the latter case, it is likely that chemistry of the depositional environment and the period of exposure to potentially variable environmental conditions will determine the nature of charcoal alteration. As production temperature rises from 300°C to 600°C charcoal carbon is increasingly hosted in polyaromatic structures of high chemical stability, and becomes increasingly homogeneous. These structures have extremely high resistance to chemical oxidation, comparable to results for ordered graphite. Similar results are obtained for charcoal produced in laboratory conditions and on open fires. In contrast charcoal exposed to environmental conditions consists of a highly carboxylated aromatic structure in which three main carbon fractions are visible in oxidation rate curves. Despite evidence of production temperatures >400°C, the majority of carbon within these charcoal samples shows more rapid oxidative degradation rates than predicted. These results suggest a smaller size of aromatic domains in the environmental charcoals, and that at least some of the samples have been subject to post-depositional alteration. This work highlights the heterogeneity in chemical forms within different charcoal samples, and the fact that at least some forms of charcoal are subject to post-depositional alteration in the environment. Further, the use of the dichromate oxidation method in this way (i.e. constructing sample oxidation rate curves), has clear utility in revealing highly detailed information regarding the

chemical structure of individual charcoal samples. Finally the results emphasize the importance of methodological approaches to charcoal characterization that integrate data from multiple analytical techniques, to improve both identification of post-depositional diagenetic processes, and understanding of the dynamic role of charcoal in depositional environments.

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Tables

Fr _{Char} samples				Env _{Char} samples			
Fr _{Char} sample code	Species	Temp (°C)	%O ₂	Env _{Char} sample code	Location	Available depositional description	Age
P-300	<i>Pinus sylvestris</i>	300	0	Env-1	Maninjau, Sumatra	Pumiceous lapilli and ash, under andisol and basaltic-andesite lapilli ¹	53400 ± 1400 ¹⁴ C yrs BP ¹
P-400	<i>Pinus sylvestris</i>	400	0	Env-2	Faial island, Azores	Lahar deposit resulting from basaltic eruptions ²	1049 ± 24 ¹⁴ C yrs BP ³
P-500	<i>Pinus sylvestris</i>	500	0	Env-3	Langanes, South Iceland	Basal fill of charcoal production pit ⁴	935 ± 35 to 960 ± 35 ¹⁴ C yrs BP ⁴
P-600	<i>Pinus sylvestris</i>	600	0	Env-4	Höskulsstaðir, North Iceland	Basal fill of charcoal production pit ⁴	895 ± 35 ¹⁴ C yrs BP ⁴
M-300	<i>Rhizophora apiculata</i>	300	0	Env-5	Toca da Bastiana, Brazil	Fluvial deposits of red sand and clay in calcareous rockshelter ⁵	129.7 ± 0.4 pMC ³
M-400	<i>Rhizophora apiculata</i>	400	0	Env-6	Oursi-hubeero, Burkina Faso ^{6,7}	Sandy soils with clay inclusions ^{6,7,8}	c. 1050 AD ^{7,8}
M-500	<i>Rhizophora apiculata</i>	500	0	Env-7	St. Peter Port, Guernsey, UK ⁹	Ephemeral post-holes and pits ⁹	6308 ± 36 ¹⁴ C years BP ⁹
M-600	<i>Rhizophora apiculata</i>	600	0	Env-8	Carvalhais, Portugal ¹⁰	Acidic soils developed on granite	Undated. Roman-period deposits
P-300-OX	<i>Pinus sylvestris</i>	300	2	Env-9	Toca Nova do Inhare, Brazil ⁵	Sand and clay deposits in calcareous rockshelter ⁵	7355 ± 40 ¹⁴ C years BP (OxA-16027)
P-400-OX	<i>Pinus sylvestris</i>	400	2	Env-10	Oursi Nord, Burkina Faso ^{6,7,8}	From settlement mound ^{6,7,8}	c.1010-1160 AD ^{6,7,8}
P-500-OX	<i>Pinus sylvestris</i>	500	2	Env-11	Killymoon, Ireland	Ashy soil overlying acid peat ¹¹	2590 ± 90 ¹⁴ C years BP ¹¹
P-600-OX	<i>Pinus sylvestris</i>	600	2	Env-12	Castro de Santiago, Portugal	Acidic soils developed on granite ¹²	2748 ± 28 ¹⁴ C years BP ³
M-300-OX	<i>Rhizophora apiculata</i>	300	2	Env-13	Pedra Furada, Brazil	Sand and clay deposits in sandstone rockshelter ^{13,14,15}	6509 ± 31 ¹⁴ C years BP ³
M-400-OX	<i>Rhizophora apiculata</i>	400	2	-	-	-	-
M-500-OX	<i>Rhizophora apiculata</i>	500	2	-	-	-	-
M-600-OX	<i>Rhizophora apiculata</i>	600	2	-	-	-	-
P-N1	<i>Pinus sylvestris</i>	Open fire	Restricted	-	-	-	-
P-N2	<i>Pinus sylvestris</i>	Open fire	Restricted	-	-	-	-

Table 1: Descriptions of Lab_{Char} and Env_{Char} charcoal samples used in this study. ¹Alloway et al., 2004; ²Cruz et al., 2006; ³Ascough et al., 2010b; ⁴Church et al., 2007; ⁵Stelman et al., 2002; ⁶Hallier and Petit, 2000; ⁷Hallier and Petit 2001; ⁸ Höhn, 2005; ⁹Sebire, 2005; ¹⁰Vieira, 2006; ¹¹Hurl, 1995; ¹²Valera, 1997; ¹³Guidon and Delibrias, 1985; ¹⁴Delibrias et al., 1988; ¹⁵Santos et al., 2003.

Bands (cm⁻¹)	Assignments
3400-3300	O-H stretching of H ₂ O
2920 and 2850	aliphatic C-H stretching
2550	H-bonded carboxylic groups
1715	C=O stretching in COOH
1605	Ionized carboxyl groups
1600-1562	C=C vibrations of aromatic structures
1510	Aromatic C=C ring stretching (lignin)
1450	Aliphatic CH deformation
1430-1420	Aromatic C=C ring stretching
1380	COO ⁻
1250	C-O stretching and O-H deformation in COOH, C-O stretching in phenol
1160	C-O-C of glycosidic links
1110	Pyranose ring carbons in cellulose
1060-1030	Aliphatic ether C-O- and alcohol C-O stretching
870	1 adjacent H deformation
810	2 adjacent H deformation
780-770	Aliphatic CH ₂ deformation
750	3-4 adjacent H deformation

Table 2: FTIR peak assignments used in analysis of spectra obtained within this study, based on published assignments from Guo and Bustin, (1998); Nishimiya et al., (1998); Moore and Owen, (2001).

Sample code	Oxidation time (hrs)	C loss (%)	$\delta^{13}\text{C}$	$\Delta\delta^{13}\text{C}$	%O	O/C	Δ O/C	
P-300	0	0.00	-27.19	0.00	28.7	0.34	-	
	0.5	41.62	-26.92	0.27	32.7	0.43	0.09	
	1	80.77	-26.73	0.46	34.4	0.46	0.12	
	2	79.47	-26.76	0.43	-	-	-	
	4	80.26	-27.59	-0.40	-	-	-	
	6	73.87	-27.21	-0.02	-	-	-	
	8	74.57	-27.51	-0.32	-	-	-	
	24	90.51	-27.56	-0.37	27.5	0.36	0.02	
	71	91.28	-26.65	0.54	-	-	-	
	120	99.30	-26.39	0.80	-	-	-	
P-400	0	0.00	-27.59	0.00	18.3	0.18	-	
	24	12.60	-27.67	-0.08	-	-	-	
	75	16.66	-27.61	-0.02	19.3	0.20	0.02	
	144	22.86	-27.62	-0.03	-	-	-	
	792	46.62	-27.64	-0.06	23.1	0.27	0.09	
P-500	0	0.00	-27.91	0.00	11.0	0.10	-	
	144	35.50	-27.52	0.39	13.6	0.15	0.05	
	504	47.85	-27.62	0.29	-	-	-	
	792	46.09	-27.62	0.29	24.4	0.29	0.16	
P-600	0	0.00	-27.86	0.00	7.0	0.06	-	
	504	13.57	-27.61	0.25	17.9	0.19	0.13	
	4176	98.51	-27.51	0.35	30.3	0.45	0.39	
M-300	0	0.00	-27.61	0.00	24.1	0.26	-	
	0.5	8.25	-26.41	1.20	23.8	0.26	0.00	
	1	41.72	-26.34	1.27	24.8	0.27	0.01	
	2	12.26	-26.48	1.13	-	-	-	
	4	15.15	-26.43	1.18	-	-	-	
	6	25.44	-26.44	1.17	-	-	-	
	8	21.98	-26.44	1.17	-	-	-	
	24	29.05	-26.35	1.26	24.7	0.28	0.02	
	72	32.71	-26.38	1.23	25.1	0.28	0.02	
	120	57.84	-27.71	-0.10	-	-	-	
	152	66.27	-27.63	-0.02	-	-	-	
M-400	0	0.00	-28.31	0.00	15.2	0.15	-	
	24	6.62	-28.40	-0.09	-	-	-	
	71	7.64	-28.21	0.10	17.7	0.18	0.02	
	144	12.60	-28.43	-0.12	-	-	-	
	792	37.21	-28.25	0.06	19.1	0.22	0.06	
	M-500	0	0.00	-28.72	0.00	10.6	0.09	-
		144	10.48	-28.67	0.05	12.4	0.11	0.02
504		7.51	-28.63	0.09	-	-	-	
792		9.27	-28.66	0.06	16.3	0.16	0.07	

M-600	0	0.00	-28.63	0.00	7.5	0.07	-
	792	8.11	-28.48	0.15	-	-	-
	4176	94.64	-26.36	2.26	33.8	0.47	0.40
P-300-OX	0.00	0.00	-27.33	0.00	28.1	0.31	-
	2.00	7.96	-27.29	0.04	26.7	0.29	-
	6.00	12.91	-27.28	0.06	-	-	-
	9.00	10.09	-27.21	0.12	-	-	-
	24.00	20.27	-27.38	-0.04	-	-	-
	71.00	20.32	-27.40	-0.07	24.3	0.28	0.03
	120.00	34.04	-27.32	0.01	-	-	-
	152.00	37.03	-27.36	-0.03	-	-	-
	267.00	62.43	-27.45	-0.12	-	-	-
	432.00	90.48	-27.61	-0.28	-	-	-
P-400- OX	0	0.00	-27.43	0.00	25.3	0.29	-
	24	2.37	-27.60	-0.17			
	75	3.78	-27.51	-0.08	26.6	0.30	0.01
	144	13.84	-27.67	-0.24			
	792	28.34	-27.62	-0.19	30.4	0.37	0.08
P-500- OX	0	0.00	-27.86	0.00	13.2	0.13	-
	144.0	28.04	-27.85	0.01	23.4	0.27	0.14
	456.0	41.46	-27.97	-0.11			
	504	51.59	-28.04	-0.18			
	792	52.42	-27.90	-0.04	24.4	0.29	0.16
	792	43.13	-27.93	-0.07			
P-600- OX	0	0.00	-28.25	0.00	6.3	0.05	-
	504	10.62	-28.05	0.20	19.4	0.20	0.14
	792	15.33	-28.03	0.22	-	-	-
M-300- OX	0	0.00	-27.49	0.00	23.29	0.26	-
	2	24.70	-27.56	-0.07	-	-	-
	6	41.57	-27.44	0.05	-	-	-
	9	36.38	-27.31	0.18	-	-	-
	24	59.57	-27.29	0.20	-	-	-
	71	47.05	-27.37	0.12	24.6	0.28	0.02
	120	76.07	-27.17	0.32	-	-	-
	150	78.97	-26.95	0.54	-	-	-
	267	90.13	-26.94	0.55	-	-	-
	432	99.23	-27.34	0.15	-	-	-
M-400- OX	0	0.00	-28.11	0.00	18.6	0.19	-
	24	8.76	-28.09	0.02	-	-	-
	71	8.18	-27.81	0.30	20.5	0.21	0.02
	144	15.83	-28.01	0.10	-	-	-
	792	36.63	-27.93	0.18	24.7	0.28	0.09
M-500- OX	0	0.00	-28.41	0.00	9.5	0.08	-
	144	7.45	-28.06	0.35	14.3	0.14	0.05
	504	11.94	-28.24	0.17	-	-	-
	792	12.23	-28.14	0.27	20.3	0.20	0.12
M-600- OX	0	0.00	-28.37	0.00	5.6	0.05	-

	504	9.93	-28.19	0.18	14.79	0.15	0.08
	792	13.11	-28.27	0.10	-	-	-
	1008	16.38	-24.4	3.97	-	-	-
P-N1	0	0.00	-27.70	0.00	9.4	0.09	-
	8	15.65	-27.77	-0.07	-	-	-
	120	14.18	-27.71	-0.01	-	-	-
	240	12.99	-27.50	0.20	24.9	0.27	0.18
P-N2	0	0.00	-24.73	0.00	9.5	0.08	-
	8	11.09	-24.84	-0.11	-	-	-
	24	5.21	-24.93	-0.20	11.2	0.10	0.02
	120	4.07	-24.83	-0.11	-	-	-
	240	3.30	-24.79	-0.06	14.9	0.14	0.06
HOPG	0	0.00	-45.23	0.00	-	-	-
	2	6.27	-45.33	-0.10	-	-	-
	6	8.57	-45.28	-0.05	-	-	-
	144	12.72	-45.32	-0.09	-	-	-

Table 3: Carbon loss (wt %), $\delta^{13}\text{C}$, %O and atomic O/C ratios of Fr_{Char} samples and HOPG with progressive K₂Cr₂O₇ oxidation.

Sample code	Oxidation time (hrs)	C loss (%)	$\delta^{13}\text{C}$	$\Delta\delta^{13}\text{C}$	%O	O/C	Δ O/C
Env-1	0	0.00	-24.45	0.00	9.15	0.09	-
	4	4.14	-24.38	0.07	-	-	-
	120	2.43	-24.58	-0.13	10.9	0.10	0.01
	744	9.25	-24.32	0.13	-	-	-
	1008	7.76	-24.39	0.06	-	-	-
	4176	46.17	-24.05	0.39	24.77	0.28	0.20
Env-2	0	0.00	-22.71	0.00	30.18	0.37	-
	4	88.88	-22.25	0.46	-	-	-
	5	88.87	-22.59	0.12	32.80	0.68	0.31
	6	93.41	-22.38	0.33	-	-	-
	8	92.97	-22.33	0.37	-	-	-
	10.3	95.09	-22.26	0.45	10.3	0.45	0.09
Env-3	0	0.00	-26.76	0.00	26.39	0.37	-
	6	6.45	-26.76	0.00	-	-	-
	24	11.75	-26.70	0.06	-	-	-
	48	32.02	-26.45	0.31	-	-	-
	72.00	47.15	-26.26	0.50	26.19	0.37	0.00
	118.5	68.15	-26.26	0.50	27.13	0.39	0.02
	242	78.80	-26.20	0.56	-	-	-
	360	87.67	-25.93	0.83	34.85	0.47	0.10
700	94.02	-26.17	0.59	-	-	-	
Env-4	0	0.00	-28.02	0.00	25.63	0.30	-
	6	21.31	-27.98	0.04	-	-	-
	24	36.01	-28.07	-0.04	-	-	-
	48	62.51	-27.95	0.07	30.32	0.39	0.09
	118.5	79.32	-28.16	-0.14	28.42	0.37	0.07
	168	82.78	-28.24	-0.22	-	-	-
	216	80.87	-27.80	0.22	-	-	-
	504	91.72	-28.59	-0.57	-	-	-
1053	94.79	-28.58	-0.55	24.04	0.30	0.00	
Env-5	0	0.00	-26.55	0.00	25.91	0.32	-
	4	51.20	-26.76	-0.21	-	-	-
	24	58.40	-26.90	-0.35	-	-	-
	48	70.77	-26.82	-0.27	-	-	-
	72	69.36	-26.91	-0.36	31.88	0.44	0.12
	118.5	79.27	-27.01	-0.46	33.10	0.43	0.11
	242	87.85	-26.99	-0.44	-	-	-
	336	92.37	-26.97	-0.42	-	-	-
1053	95.88	-27.00	-0.45	-	-	-	
Env-6	0	0.00	-24.90	0.00	22.19	0.25	-
	4	15.14	-24.26	0.64	-	-	-
	24	22.09	-24.22	0.68	-	-	-
	48	24.66	-24.36	0.54	-	-	-
	72	35.07	-24.08	0.83	25.41	0.31	0.06

	120	40.21	-24.08	0.83	28.47	0.35	0.10
	242	58.66	-24.06	0.85	-	-	-
	336	79.92	-24.70	0.20	-	-	-
	504	78.85	-24.49	0.41	-	-	-
	700	84.20	-24.76	0.15	-	-	-
	840	92.79	-24.63	0.27			
	1053	99.35	-24.48	0.42	31.34	0.41	0.16
Env-7	0	0.00	-26.90	0.00	34.72	0.41	-
	6	26.08	-26.75	0.14	-	-	-
	12	32.43	-26.77	0.12	-	-	-
	24	43.10	-26.65	0.25	-	-	-
	72	69.50	-26.31	0.58	37.97	0.53	0.12
	118.5	79.97	-26.51	0.39	34.00	0.45	0.04
	242	88.45	-26.35	0.55	-	-	-
	336	94.44	-27.01	-0.11	-	-	-
	700	97.87	-26.63	0.27	-	-	-
	1053	96.75	-27.00	-0.10	28.92	0.48	0.07
Env-8	0	0.00	-25.91	0.00	34.31	0.40	-
	6	26.49	-25.67	0.24	-	-	-
	12	33.92	-25.61	0.30	-	-	-
	24	35.96	-25.83	0.08	-	-	-
	72	60.02	-25.14	0.77	37.05	0.52	0.11
	118.5	83.92	-24.97	0.94	30.84	0.44	0.04
	336	97.25	-25.39	0.52	-	-	-
	1053	98.04	-26.42	-0.51	17.61	0.45	0.05
Env-9	0	0.00	-27.79	0.00	28.52	0.33	-
	4	13.05	-27.90	-0.10	-	-	-
	24	17.67	-27.82	-0.03	-	-	-
	72	27.04	-27.92	-0.13	31.31	0.38	0.05
	118.5	36.23	-27.81	-0.01	24.37	0.29	-0.04
	242	37.61	-27.76	0.03	-	-	-
	336	48.29	-27.87	-0.07	-	-	-
	504	49.11	-27.86	-0.07	-	-	-
	700	48.94	-27.93	-0.14	-	-	-
	720	46.24	-27.91	-0.12	-	-	-
	1008	36.92	-28.01	-0.21	23.27	0.27	-0.06
Env-10	0	0.00	-24.65	0.00	34.96	0.37	-
	4	19.58	-24.64	0.00	-	-	-
	24	24.28	-24.69	-0.04	-	-	-
	48	34.37	-24.83	-0.19	-	-	-
	72	64.63	-24.45	0.20	36.26	0.58	0.20
	118.5	67.95	-24.48	0.17	23.45	0.29	-0.08
	242	78.34	-24.65	0.00	-	-	-
	336	92.75	-24.62	0.03	-	-	-
	504	91.07	-24.74	-0.09	-	-	-
	700	98.96	-25.20	-0.56			
	1053	97.90	-25.43	-0.79	8.15	0.39	0.01
Env-11	0	0.00	-25.94	0.00	29.13	0.33	-

	6	15.66	-25.87	0.07	-	-	-
	12	23.66	-25.84	0.11	-	-	-
	24	27.16	-25.78	0.16	-	-	-
	72	32.92	-25.83	0.11	27.28	0.35	0.02
	118.5	50.85	-25.85	0.10	30.29	0.38	0.05
	242	68.39	-25.90	0.04	-	-	-
	336	68.64	-26.08	-0.14	-	-	-
	700	77.67	-26.11	-0.17	-	-	-
	1053	74.01	-26.11	-0.17	27.62	0.33	0.00
Env-12	0	0.00	-23.58	0.00	28.81	0.33	-
	6	22.32	-23.49	0.08	-	-	-
	12	28.91	-23.44	0.14	-	-	-
	24	28.79	-23.29	0.28	-	-	-
	72	39.84	-23.26	0.31	23.95	0.29	-0.04
	120	47.46	-23.05	0.53	23.22	0.27	-0.06
	242	70.55	-25.30	-1.72	-	-	-
	456.0	74.39	-25.60	-2.03	-	-	-
	504	83.67	-25.81	-2.23	-	-	-
	700	87.52	-26.09	-2.52	-	-	-
	840	94.93	-25.89	-2.32	-	-	-
Env-13	0	0.00	-26.83	0.00	32.81	0.35	-
	4	24.00	-26.76	0.06	-	-	-
	120	46.91	-26.69	0.14	24.20	0.29	-0.07
	336	73.13	-26.62	0.21	-	-	-
	700	85.90	-26.61	0.22	-	-	-
	1053	76.13	-26.59	0.23	36.65	0.53	0.17

Table 4: Carbon loss (wt %), $\delta^{13}\text{C}$, %O and atomic O/C ratios of Env_{Char} samples with progressive $\text{K}_2\text{Cr}_2\text{O}_7$ oxidation.

TABLES

Table 1: Descriptions of Lab_{Char} and Env_{Char} charcoal samples used in this study.

¹Alloway et al., 2004; ²Cruz et al., 2006; ³Ascough et al., 2010b; ⁴Church et al., 2007; ⁵Steelman et al., 2002; ⁶Hallier and Petit, 2000; ⁷Hallier and Petit 2001; ⁸Hohn, 2005; ⁹Sebire, 2005; ¹⁰Vieira, 2006; ¹¹Hurl, 1995; ¹²Valera, 1997; ¹³Guidon and Delibrias, 1985; ¹⁴Delibrias *et al.*, 1988; ¹⁵Santos *et al.*, 2003.

Table 2: FTIR peak assignments used in analysis of spectra obtained within this study, based on published assignments from Guo and Bustin, (1998); Nishimiya et al., (1998); Moore and Owen, (2001).

Table 3: Carbon loss (wt %), $\delta^{13}\text{C}$, %O and atomic O/C ratios of Fr_{Char} samples and HOPG with progressive $\text{K}_2\text{Cr}_2\text{O}_7$ oxidation.

Table 4: Carbon loss (wt %), $\delta^{13}\text{C}$, %O and atomic O/C ratios of Env_{Char} samples with progressive $\text{K}_2\text{Cr}_2\text{O}_7$ oxidation.

FIGURES

Figure 1A: FTIR of Pine Fr_{Char} with progressive K₂Cr₂O₇ oxidation showing changes in samples produced at 300°C (above) and 600°C (below). Hours of oxidation are indicated alongside spectra. Unoxidized (i.e. 0 hrs) spectra for P-300 and P-600 are described in Ascough et al., 2011.

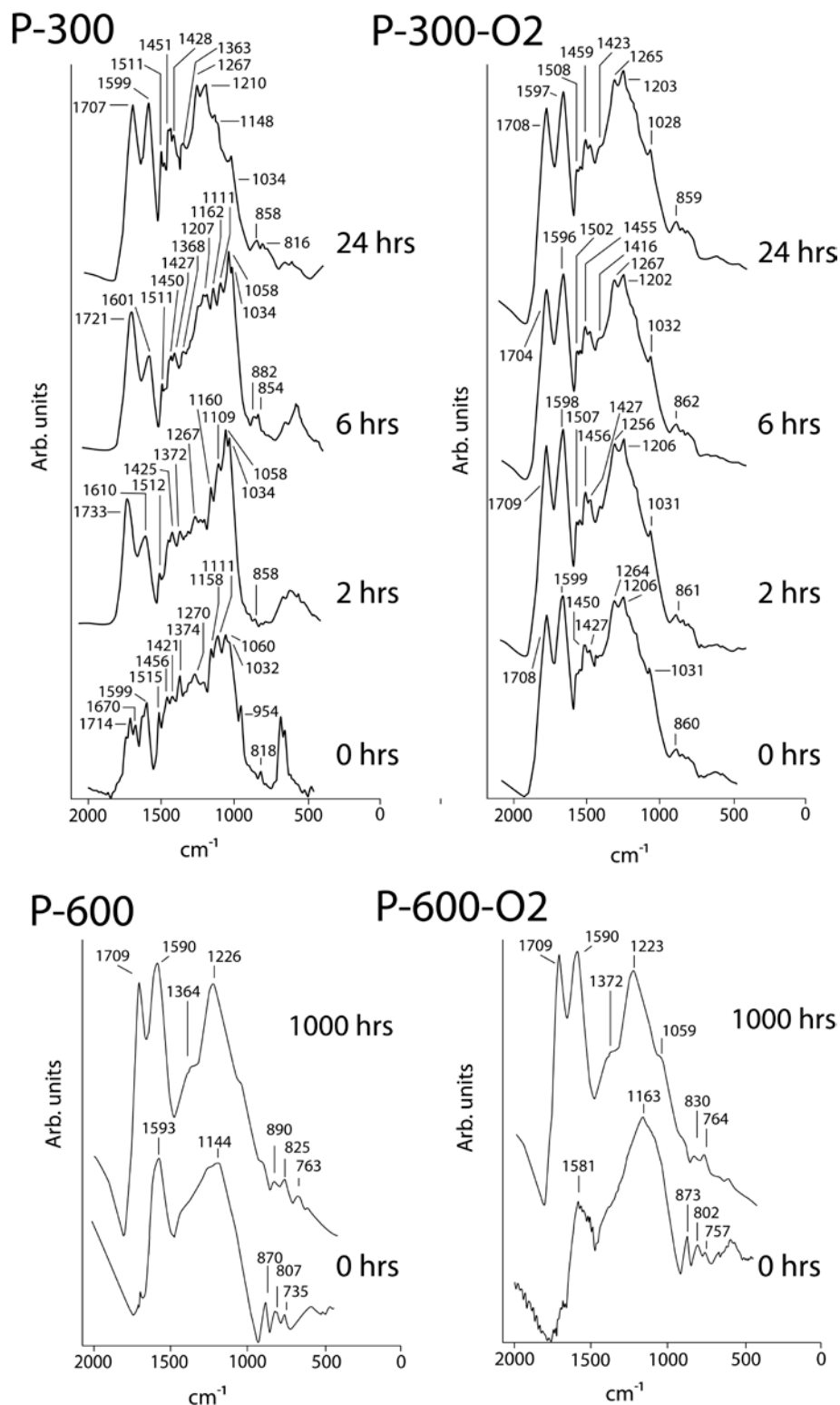


Figure 1B: FTIR of Mangrove Fr_{Char} with progressive K₂Cr₂O₇ oxidation showing changes in samples produced at 300°C (above) and 600°C (below). Hours of oxidation are indicated alongside spectra. Unoxidized (i.e. 0 hrs) spectra for M-300 and M-600 are described in Ascough et al., 2011.

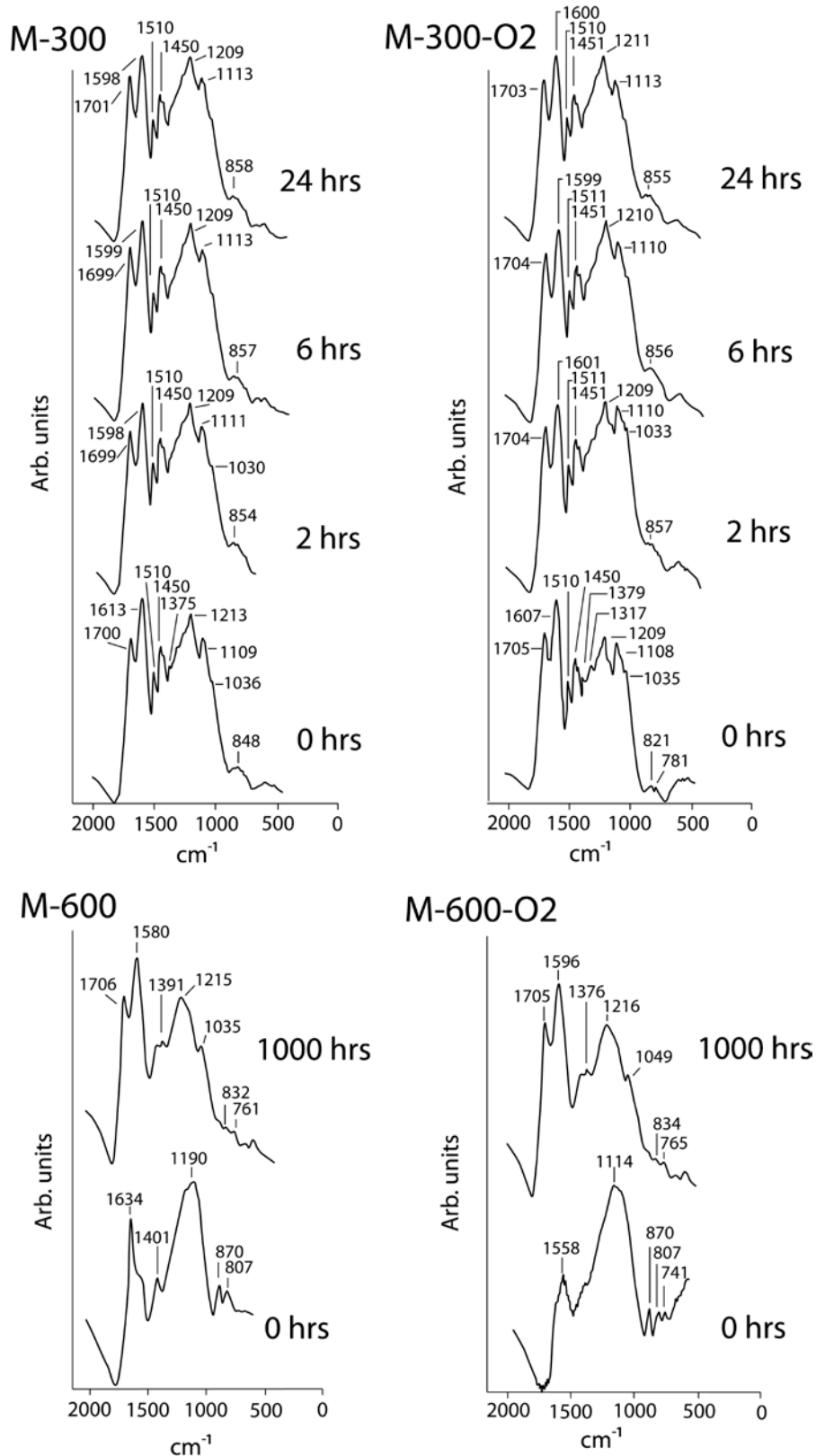
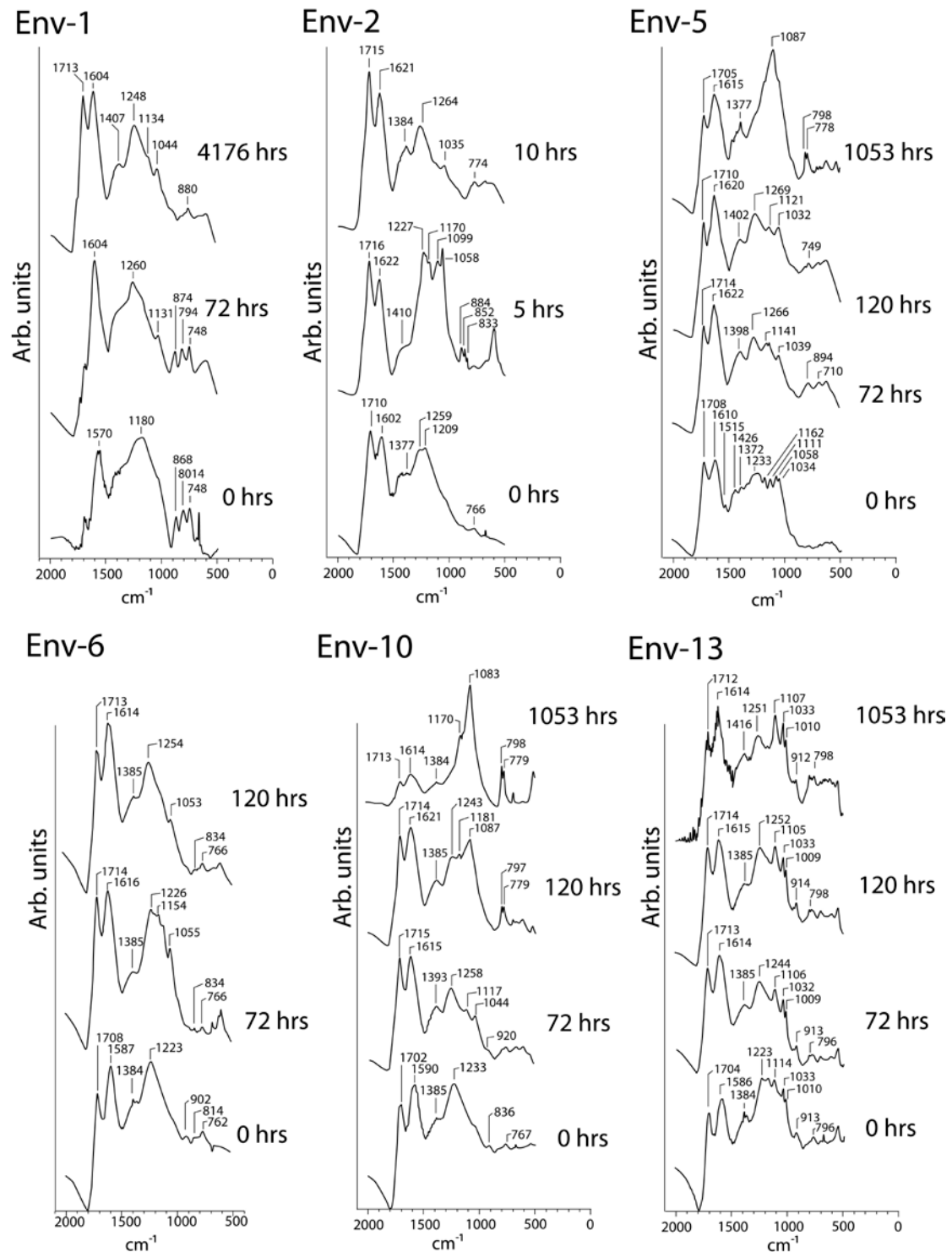


Figure 1C: FTIR of Env_{Char} with progressive K₂Cr₂O₇ oxidation. Hours of oxidation are indicated alongside spectra. Unoxidized (i.e. 0 hrs) spectra of Env-1, Env-2, Env-5 and Env-6 are described in Ascough et al., 2011.



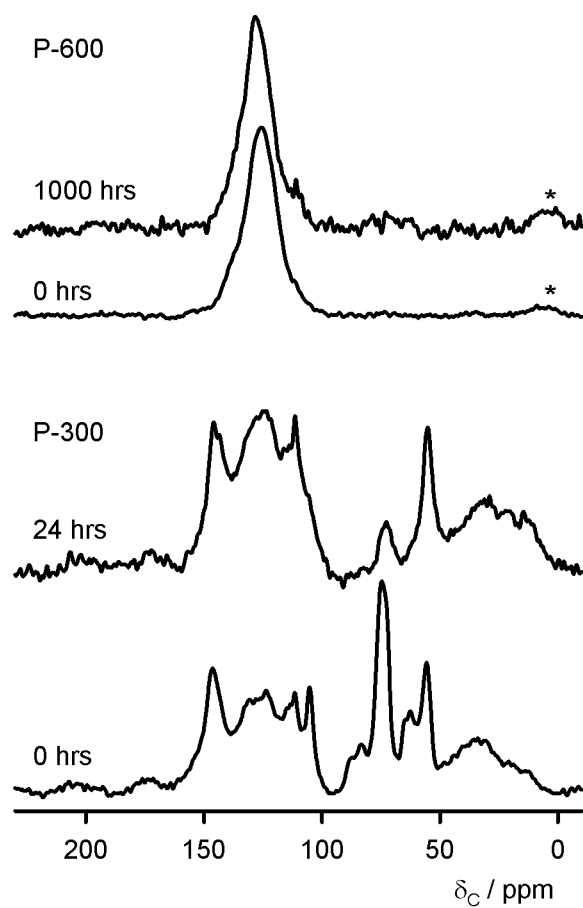


Figure 2A: ^{13}C -CPMAS NMR spectra of Pine Fr_{Char} produced under N_2 at 300°C (bottom) and 600°C (top) showing unoxidized samples (0 hrs) and samples following progressive $\text{K}_2\text{Cr}_2\text{O}_7$ oxidation. Spinning side bands are indicated by *.

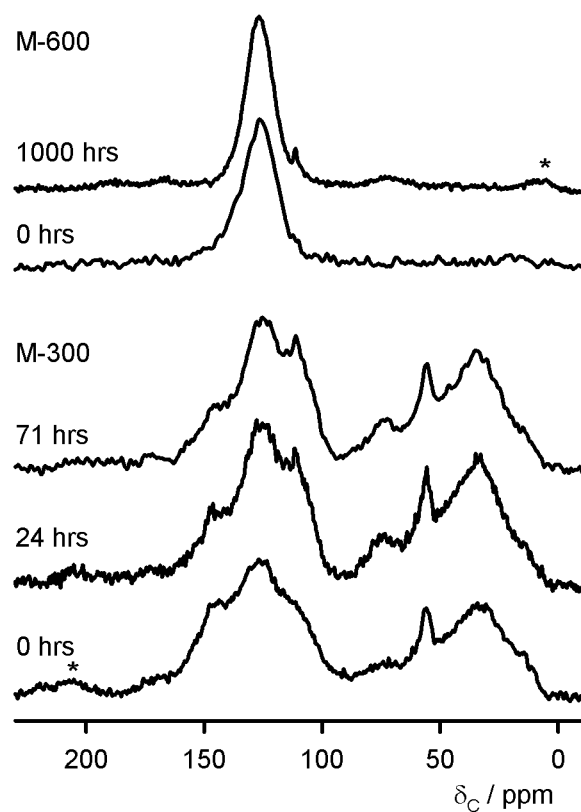


Figure 2B: ^{13}C -CPMAS NMR spectra of Mangrove Fr_{Char} produced under N_2 at 300°C (bottom) and 600°C (top) showing unoxidized samples (0 hrs) and samples following progressive $\text{K}_2\text{Cr}_2\text{O}_7$ oxidation. Spinning side bands are indicated by *.

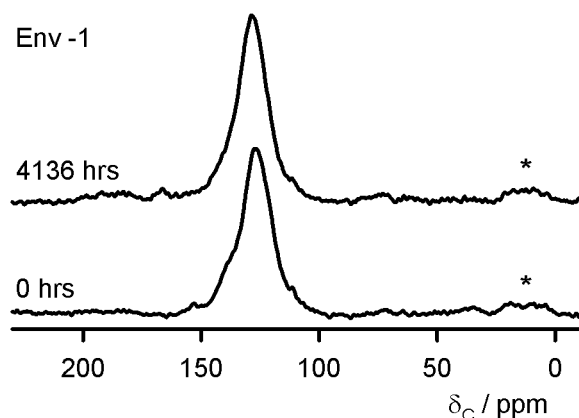


Figure 2C: Env_{Char} ^{13}C -CPMAS NMR spectra (Env-1 and Env-2) showing unoxidized samples (0 hrs) and samples following progressive $\text{K}_2\text{Cr}_2\text{O}_7$ oxidation. Spinning side bands are indicated by *.