Hydropyrolysis as a new tool for radiocarbon pretreatment and the quantification of black carbon.

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Abstract

The first results concerning the potential of hydrogen pyrolysis (hypy) as a new tool for the quantification and isolation of Black Carbon (BC) for radiocarbon analysis are reported. BC is a highly stable form of carbon, produced during pyrolysis of biomass to materials such as charcoal. Isolation and quantification of this component is therefore of great interest in radiocarbon measurement, particularly for more ancient samples, where contamination issues become more critical. Hypy has been demonstrated to reliably separate labile and refractory carbonaceous sample components for engineering and geological applications, but its potential in ^{14}C geochronological investigation has previously been unexplored. Here, we test the hypy technique using a selection of soil standard samples and ancient charcoals from deposits of geological and archaeological significance. The results show that hypy can effectively and reproducibly isolate different carbon fractions within a variety of sample types and thus has the potential to provide a rapid and robust pre-treatment technique for radiocarbon analysis. Hypy has the additional advantage that the non-BC fraction removed from a sample can be quantitatively collected for subsequent further analysis. The technique represents a promising new approach not only for ensuring reliable decontamination of

pyrogenic carbon samples prior to radiocarbon dating, but also for BC quantification in a variety of environmental matrices.

Keywords

Black Carbon, Hydropyrolysis, Radiocarbon, charcoal

1. Introduction

Black Carbon (BC) is produced from the thermal degradation of biomass under conditions of restricted oxygen (pyrolysis), a process which transforms the starting material into a range of products, including soot, char and charcoal (Preston and Schmidt, 2006). As biomass undergoes pyrolysis, the H, N, O, S content of the material decreases and the original molecular carbon structure is rearranged into condensed aromatic ring configurations (Tang and Bacon, 1964; Eckmeier *et al*., 2007), which are highly stable, and hence potentially resistant to environmental degradation. BC is therefore defined chemically as having both high aromaticity and high resistance to oxidative degradation, with estimates for the half-life of pyrolyzed carbon in soils extending to 5-7ky (Preston and Schmidt, 2006). BC exhibits both global distribution and locally high abundance in soils and sediments, for example, in some soils up to 35% of total organic carbon content is comprised of charred biomass (Skjemstad *et al*., 2002). BC also plays a dynamic role within soil systems, influencing pedogenic development, and duration of BC storage within soils appears influenced by factors of climate, deposition environment, and land use (Czimczik and Masiello, 2007). This means that BC is an important source of geochronological data, commonly submitted for radiocarbon (^{14}C) measurement, in the form of both isolated samples of pyrolysed material (e.g. charcoal fragments), and as a component within bulk samples (e.g. soils, marine sediments and aerosols).

The removal of extraneous carbonaceous contaminants is essential prior to ^{14}C measurement, and standard pre-treatment for pyrogenic carbon material involves sequential extraction with acid and base reagents (ABA method), to remove soil carbonates and organic acids. While contaminant removal is non-selective (Santos *et al.,* 2001), exact pre-treatment conditions vary between laboratories, and it is not routine to empirically assess the amount or chemical composition of the contaminants removed. The ABA treatment appears rapid and effective for the majority of samples. However, elimination of contamination becomes more critical as sample age increases, and confidence in the measured ^{14}C activity of material closer to the limit of the ^{14}C method depends upon confidence in the ability of a pre-treatment to exhaustively remove any extraneous carbonaceous contamination. In some environments the ABA pre-treatment appears not to successfully remove all contaminants (Gillespie *et al*., 1992). For example, analysis of charcoal associated with deposits from a tropical volcano indicated only partial removal of residue from the decomposition of modern plant rootlets using the ABA technique (Harkness *et al*., 1994). In addition, pyrolysed biomass such as charcoal has a high affinity for, and will readily adsorb, compounds such as phenols and polycyclic aromatic hydrocarbons (Cornelissen and Gustafsson, 2004; Sander and Pignatello, 2005; Wang *et al*., 2001). The magnitude of organic chemical sorption by BC-containing materials is non-linear, therefore may be considerably larger than that exhibited by other soil organic matter (Cornelissen *et al*., 2005). Soil microbial communities also interact with pyrolysed biomass in soils (e.g. Warnock *et al*., 2007), with enhanced soil biota activity suggested as a result of factors such as availability of carbon and nutrients sorbed onto the charcoal surface (Pietikäinen *et al*., 2000), or through the provision of micro-habitats within the char structure itself (Wardle *et al*., 1998). In such cases, exhaustive removal of all contaminants is time-consuming, and it may be difficult to remove components sorbed or weakly bonded to the sample matrix without completely destroying the sample.

As BC represents carbon fixed by pyrolysis of biomass at the time of an event of interest for dating, the ability to isolate and measure this component is of considerable significance for ^{14}C geochronology. This is applicable both for age measurement in terms of palaeoenvironmental events and in the form of tracer studies for environmental processes, for example, in quantification of sedimentary turnover rates. An alternative pre-treatment for samples older than 30-35 ka BP, or where conventional ABA methods do not satisfactorily remove contaminants, is to remove all material apart from the most chemically resistant fraction. One such method replaces the final acid wash of the ABA treatment with wet oxidation, followed by stepped combustion (ABOX-SC). This technique allows analysis of the most chemically resistant fraction of carbonaceous samples (Bird *et al*., 1999), and has been used in age measurement of samples up to ~55 ka BP (Santos *et al*., 2001; Turney *et al*., 2001). Issues with this method include the potential release of volatile sulphur compounds during evolution of sample CO_2, resulting from the use of H_2SO_4 in the oxidation step, inhibiting graphitization of the sample (Santos *et al*., 2001). The main issue with the ABOX-SC method however, is the difficulty of identifying the point at which contaminants are removed and further oxidation results in degradation of the BC structure itself. The amount of material isolated as BC via chemical oxidation varies depending upon the source material and applied oxidation time (Knicker *et al*., 2007). For example, procedural variations in oxidation by acidified dichromate for BC isolation within a systematic international inter-comparison study resulted in BC determinations from 1.1-8.0 and 0.6-2.2 g kg^{-1} in two soils, along with variations in internal reproducibility of a factor of at least 2 (Hammes *et al*., 2007). The effective use of BC for ^{14}C measurement therefore depends upon the ability to reliably isolate and analyse this material from a range of environmental matrices. Attempts to improve current analytical techniques are complicated by the fact that methodological developments for BC isolation are ongoing, and that various existing methodologies define BC according to different criteria, depending upon the part of the pyrogenic carbon continuum they target (Preston and Schmidt, 2006). Some methods may also result in methodological artefacts, for example, Simpson and Hatcher (2004) found that a thermal oxidative method for BC quantification inadvertently produced a component of pyrolysed organic matter subsequently defined as BC during analysis of initially BC-free material. Research aims have therefore included the development of methodologies that reduce the potential for artefacts and allow greater accuracy in BC quantification (e.g. Gelinas *et al*., 2001).

Extensive research benefits are therefore offered by a technique that can effectively and reproducibly isolate and quantify purified BC from a wide range of sample matrices. In this paper, we explore the potential of a new method which holds great promise in this regard, known as hydropyrolysis (hypy). Hypy uses pyrolysis assisted by high hydrogen pressures (>10 MPa) with a dispersed sulphided molybdenum (Mo) catalyst to separate labile and refractory carbonaceous sample components. This process has been used extensively in analysis of terrestrial kerogens where overall conversions of close to 100% are achieved for thermally labile material (e.g. Roberts *et al*., 1995), the principal product being a dichloromethane-soluble oil. Further, it has been shown that the hydrocarbon products of hypy are released in high yields (Love *et al*., 1997), with the advantage that it should be possible to identify and characterize the non-BC contaminants in samples at a molecular level, including analysis of ^{14}C activity. Because stereochemical rearrangements accompanying hypy are minimal due to the high pressure hydrogen, the neoformation of BC that occurs in normal thermal oxidation is largely suppressed, meaning that interference from formation of BC during the analytical procedure should not prove to be a major issue (Love *et al*., 1995).

In general, hypy offers a potential means to discriminate between bound and adsorbed organic species. As a result of this, the technique has been used to remove adsorbed products, facilitating analysis of organic carbon in samples even up to Archaean age (Brocks *et al*., 2003). Thus far, however, the potential application of hypy for the quantification and isolation of BC for ^{14}C measurement remains unexplored. In this study, we have used a range of samples containing BC to assess the use of hypy for this purpose, of various antiquities and from different soil matrices. One key factor is whether it is possible to determine the operational conditions under which removal of the labile organic matter is complete. At this point, further hydrogen pyrolysis would result in degradation of the purified BC itself via hydrogasification. We have therefore assessed the reproducibility and reliability of the method to isolate BC from soils and charcoal, and used ^{14}C measurement of the hypy residue and removed products to test its potential utility as a pre-treatment procedure for ^{14}C analysis of charcoal.

2. Materials and methods

2.1. Samples

Information on the samples selected for this study is provided in table 1. These include three ancient charcoals obtained from natural and archaeological deposits, two of which are from deposits of key geological and archaeological significance, close to the radiocarbon dating boundary, with previously established ^{14}C ages. The first of these charcoal samples (MA) was recovered *in situ* from paroxysmal flow deposits source from the Maninjau caldera in west-central Sumatra. Isothermal plateau and diameter corrected fission-track techniques place the flow deposits at 50,000 ± 3000 BP (Alloway *et al*., 2004). For MA, the previous ^{14}C measurements included pre-treatment by conventional ABA and ABOX-SC pre-treatment, giving ages of 51,100 to 52,300 ^{14}C BP, and earlier assessments of infinite ages >40,000 ^{14}C BP (Table 1).

The second charcoal sample, CHA, was recovered from a hearth deposit in the Megaceros gallery of Chauvet Cave, in the Ardeche Valley of France. Human activity in the cave included the oldest parietal art thus recorded, dated to ca. 32,000 years BP (Clottes et al., 1995, Valladas et al., 2001 and Valladas et al., 2005), and along with charcoal, associated deposits containing animal skeletal remains, animal and human footprints, and flint and ivory artefacts (Garcia, 2005 and Geneste, 2005). The charcoal sample obtained from material excavated at Chauvet Cave (CHA) had previously been subjected to ^{14}C measurement as part of a laboratory intercomparison exercise (Cuzange *et al*., 2007), as part of which the ABOX-SC pre-treatment methodology was used for some measurements, yielding ages of 32,350 ± 210 ^{14}C BP (OxA-X-2130-47) for the oxidation stage only, 32,080 ± 200 ^{14}C BP (OxA-X-2131-14) for oxidation followed by 300°C pre-combustion and 31,810 ± 190 ^{14}C BP (OxA-X-2130-48) for oxidation followed by 630°C pre-combustion. The results of multiple ^{14}C measurements on charcoal samples from the hearth from which CHA was sampled yielded an average age of 32,030 ± 120 ^{14}C BP (Cuzange *et al*., 2007).

The final charcoal sample, CAS, was recovered from deposits at the site of Castro de Santiago, a hilltop settlement with enclosures, located in Fornos de Algodres, Guarda district, central Portugal. This sample itself had not previously been ^{14}C-dated, however attached enclosures at the archaeological site from which the material was obtained have been established to date to around 5000-4500 calendar years before present (Valera, 1997).

Along with charcoal, three modern soil samples were selected for analysis (table 1), in order to test the suitability and reproducibility of hypy for quantifying soil BC, using well characterized standard soil material. Two of these (VER and MO), were produced and distributed under the auspices of the International Steering Committee for Black Carbon Reference Materials. VER is a vertisol, a sandy clay soil, collected at 0-10 cm depth from the region of Toowoomba in Queensland, Australia by CSIRO Land & Water, Australia, and is described in detail in Skjemstad *et al*., (1999) and Schmidt *et al*., (2001). MO is a mollisol, a sandy soil, developed on loess in the region of Hildesheim-Braunschweig, northern Germany. The sample was collected at 20-60cm depth, by the University of Cologne, and is described in detail in Schmidt *et al*. (1999).

The BC content of these two soils was measured at several laboratories as part of the BC international inter-comparison where a range of methods were used to quantify BC (Hammes *et al*., 2007). As mentioned above, the results varied widely depending upon methodological conditions, however overall MO was found to have slightly lower BC content than VER (Table 1). The final soil sample (BGS), is a silty clay soil, from an area of anthropogenically disturbed ground in Glasgow, Scotland. The nature of the disturbance included ash deposition, indicating recent burning, and therefore a BC contribution to the sample composition. This sample was collected at 0-15cm depth by the British Geological Survey in 2001 (Rawlins et al., 2008), where the BC content (24.3 g kg^{-1}) was determined by a modified chemothermal oxidation method (after Kuhlbusch, 1995).

2.2. Hypy procedure

Fixed bed hypy tests were performed using the apparatus shown in figure 1, with the products collected in a silica filled trap (Meredith *et al*., 2004) immersed in an ethanol dry ice slush trap at -72˚C. The procedure is described in detail in Love *et al*., (1995; 1997). Briefly, the samples were first loaded with the Mo catalyst (5% by weight) using an aqueous/methanol 0.2M solution of ammonium dioxydithiomolybdate [$(NH_4)_2MoO_2S_2$], and then pyrolysed with resistive heating from 50˚C to 250˚C at 300˚C min^{-1}, and then from 250˚C to the final temperature (between 400 and 600 °C) at 8 °C min^{-1}, under a hydrogen pressure of 15 MPa. A hydrogen sweep gas flow of 5 L min^{-1}, measured at ambient temperature and pressure, ensured that the products were quickly removed from the reactor vessel. Three replicate tests to a final hold temperature of 500 °C were performed on the MO soil sample to assess reproducibility of the hypy technique.

2.3. Determination of non-BC removal using hypy

Tests were performed in order to ascertain whether it was possible to observe a plateau with increasing temperature corresponding to a temperature interval after the removal of labile organic matter is complete (i.e. non-BC material, mainly lignocellulosic) and before the onset of hydrogasification of the BC itself to methane (e.g. Suzuki *et* al., 1986; Bolton *et al*., 1987; Xua *et al*., 2003). This involved monitoring the residual Total Organic Carbon (TOC) content of VER and BGS reference soils and charcoal sample MA as a function of the peak temperature used in each hypy test. Hypy temperature was varied between 400 and 600 °C at increments of 25 °C for the soils and between 500 and 600 °C for the charcoal. For MA, the total mass loss of the sample was determined for each experiment. The TOC of samples were measured using a CO_2 coulometer (UIC® Coulometrics Inc., IL, USA), which measures the CO_2 generated by combustion of the sample at 1000 °C in a stream of oxygen by titration against ethanolamine. For each sample the average of two replicate analyses was taken.

2.4. Hypy procedure for ^{14}C measurement

After the hypy treatment the sample residue and the hypy product, cryogenically collected on silica (i.e. removed contamination), were AMS dated at the ORAU (Oxford Radiocarbon Accelerator Unit), University of Oxford. ^{14}C measurements were also made of aliquots of the untreated charcoal and charcoal treated with 0.5M HCl for decarbonation (as described below). For $\delta^{13}C$ measurements, samples were combusted and analyzed using a Europa Scientific IRMS system interfaced to a Roboprep CHN sample converter unit, operating in continuous flow mode using helium as the carrier gas. Stable isotope ratios are expressed in ‰ relative to vPDB where mass spectrometric precision is ± 0.2‰. The ^{14}C content of charcoal reflects that of atmospheric sources at the time the plant grew, and thus reflects a relatively constrained time interval. In this instance, the event of interest for dating, (i.e. the date of plant tissue formation), corresponds to a single, constrained and hence 'dateable' event. This contrasts with the BC component of the soil samples, as it is likely that this represents a mix of inputs from different sources over an extended but unknown period. Therefore, while the soil samples represent well-characterized standard materials, they are otherwise uncontextualized, limiting our ability to interpret a ^{14}C measurement of these samples following hypy in a meaningful manner.

The charcoal samples for ^{14}C determination were crushed to pass a 500 mm mesh, and an aliquot of the crushed material (i.e. with only physical treatment) was taken for dating as representative of the untreated sample. The remaining sample material was then placed in 0.5M HCl overnight to remove soil carbonates. Following decarbonation the sample material was washed three times in deionized water before drying to constant weight at 50°C. An aliquot of the decarbonated charcoal was subjected to standard ABA pre-treatment at the University of Oxford (c.f. Wild et al., 2008). This consists of an acid wash to remove sediment carbonates, a base wash to remove organic acid contaminants such as humic acids and a final acid wash (to remove any atmospheric CO_2 which may have been absorbed by the sample during the base wash). In between each wash the samples were thoroughly rinsed with ultrapure water.

Aliquots of the decarbonated charcoal samples were also taken for hypy treatment. The heating regime was designed to ensure optimum removal of all lipids, proteins and lignocellulosic material in the sample, leaving only the purified BC fraction, and comprised heating as described above with final holding at 600°C for two minutes. It is possible that at the higher temperature, some hydrogasification of the BC structure itself could occur but, as will be discussed, the extent of hydrogasification at this temperature is not considered to be significant. Instead, a higher temperature, more aggressive hypy regime was targeted at removal of labile carbonaceous sample fractions, rather than BC quantification. The weights pyrolysed for MA, CAS and CHA were 306, 273 and 84 mg respectively, and to each sample catalyst was loaded at 5% weight Mo.

3. Results

3.1 BC determination via hypy

The change in residual TOC as a function of temperature for the VER and BGS reference soils and the MA charcoal is presented in table 2 and figures 2 and 3. Mass losses during hypy of the soil samples were c. 2-3% w/w. Figure 2 shows the same trend of decreasing carbon content until 550°C for VER and 525°C for BGS, corresponding to the loss of carbon from the labile (i.e. non-BC) organic matter in the soil. Following this phase a plateau in TOC is reached. This is consistent with other hypy studies for lignocellulosic material which has indicated that up to 100% conversion to volatile products is achieved by approximately 500°C (Rocha et al., 1999). At 600°C, following the plateau phase, there is the beginning of a further loss of carbon which marks the onset of char hydrogasification to yield methane. The residual TOC content over the plateau region is taken as the BC content of the sample material, and represents the conditions under which the total BC portion of a sample may be recovered. For VER at 550°C this suggests a BC content of 6.6 g kg^{-1} which is consistent with, but at the upper end of values obtained for this sample in the BC inter-comparison study (e.g. 4.7±2.9 g kg^{-1} for dichromate oxidation (Hammes *et al*., 2007)). For the BGS sample at 550°C the estimated BC content is 28.5 g kg^{-1}, which is comparable with previous BC determination for this sample of 24.3 g kg^{-1}. These results provide strong evidence that at temperatures above c.500^{0}C non-BC sample components are effectively removed.

Clearly, depending where a particular sample lies on the broad continuum of compositions, some weight loss might be anticipated during hypy, especially those samples that have not been subjected to high temperature during pyrolysis. This is supported by the tests on the MA charcoal sample, where sample weight loss during hypy increases from 14.1% by 500^{o}C to 26.8% by 600^{o}C where it then appears to level off (figure 3). Much of the weight loss below 500^{o}C is due to oxygen removal which gives rise to the increase in the TOC content relative to the initial (catalysed) sample (table 2) but some carbon loss from the sample itself has also occurred. Most of the mass loss of the MA sample between 500 and 575^{o}C is also due to oxygen as indicated by the fairly constant level of TOC remaining over this temperature range. However, a small quantity of tar was collected, which may be derived from the decomposition of highly aromatic humic acids (Haumaier and Zech, 1995). The apparent plateau in the MA sample still evident at 600^{o}C could represent a delayed onset of hydrogasification in relation to the two soil samples. The uncertainty in the BC determination arising from this extended plateau however is clearly very small compared to the high variations described earlier for oxidative procedures.

3.2 Reproducibility

The TOC content of the uncatalyzed MO soil sample prior to hypy treatment was 2.00%. After the hypy treatment, triplicate analyses of the sample TOC content gave a final average value of 0.76 ± 0.02% for identical run conditions of a single sample. This indicates a high degree of measurement precision can be achieved with the hypy methodology, which compares favourably with that achieved in other studies with a variety of BC quantification methodologies (e.g. Schauer *et al*., 2003; Schmid *et al*., 2001; Hammes *et al*., 2007).

3.3. ^{14}C analysis

The results of the ^{14}C measurements are listed in table 3. Results for the MA charcoal residue extracted by hypy (51,200 ± 1100 ^{14}C BP; figure 4(A)) are consistent with previous measurements of this sample (Table 1). ^{14}C measurement of the untreated sample is also consistent with these analyses, demonstrating that for this sample, the level of environmental contamination does not significantly affect its ^{14}C age. Results for the aliquot of MA (OxA-16319; 46,600 ± 700 ^{14}C BP) that had been subject to 0.5M HCl digestion and deionized H_2O washing prior to ABA pre-treatment and ^{14}C measurement do however suggest either that this (0.5M HCl digestion), or the ABA treatment itself, introduces trace amounts of contamination. Analysis of the product of hypy (retained on silica following removal from the pyrogenic carbon sample) gives a ^{14}C age of 37,450 ± 750 ^{14}C BP. This indicates that carbon contamination younger than the ^{14}C age of the initial sample, albeit present in small amounts, is removed in the hypy treatment.

^{14}C measurement of the untreated sample of CHA (figure 4(B)) shows that, in common with MA, environmental contamination by younger carbon does not significantly affect the bulk sample $^{14}C/^{12}C$ ratio, as this measurement, 32,370 ± 180 BP (OxA-V-2211-17), is consistent with previous determinations performed within the laboratory intercomparison exercise (Cuzange *et al*., 2007). This conclusion was also drawn by Cuzange *et al*., (2007), following

^{14}C measurement of the alkali-soluble fraction of Chauvet Cave charcoals, which were not found to be significantly different from the purified charcoal following conventional pre-treatment. Measurement of the aliquot of CHA subject to 0.5M HCl treatment gives an age of 31,990 ± 180 BP (OxA-17090) following ABA pre-treatment and 31,150 ± 250 BP (OxA-V-2211-16) following hypy treatment. The products of hypy extraction of the CHA sample on silica were dated to 28,050 ± 310 BP (OxA-V-2198-50), again significantly younger than that of the hypy residue, indicating selective removal of contamination present in small amounts. It is important also to note that, as well as younger contamination, samples may also be affected by older exogenous carbon, with a lower ^{14}C activity to that of the sample. In the case of CHA, the untreated ages appear slightly older than those subject to pre-treatment, which may indicate the presence of older, possibly geological, material.

Analysis of the high ^{14}C activity Holocene charcoal sample (CAS), presented in figure 4(C), showed that again, environmental contamination present in the sample does not appear to be sufficient to influence the ^{14}C age, as the age of the untreated sample (2732 ± 29 BP) is within analytical error of the treated sample ages. In this instance, aliquots of CAS subject to 0.5M HCl treatment give similar ages whether treated by ABA (2723 ± 28 BP) or hypy (2748 ± 28 BP). In addition, the age of the material extracted by hypy onto silica (2732 ± 28 BP) is also similar to that of the purified charcoals. This indicates that the non-BC material in this sample is either not of a significantly different ^{14}C activity to that of the BC material fixed by pyrolysis during sample formation, or is present in trace quantities insufficient to influence the measured age of this more recent age sample.

4. Discussion

The results show the potential for the hypy methodology to effectively isolate labile and resistant carbon fractions, from both individual samples of pyrolysed biomass and complex BC-containing matrices such as soil. The TOC profiles for soil and charcoal samples show that it is possible to identify a set of conditions for hypy analysis under which lignocellulosic and other easily convertible organic carbon material (e.g. lipids, proteins) are fully removed, but at which degradation of the resistant BC component of the sample has not yet commenced. This in turn appears to facilitate the removal of contaminating carbon compounds with a different ^{14}C activity to that of the hypy residue sample fraction, as seen in the ^{14}C measurement of the products removed from the MA and CHA samples onto silica during hypy treatments, which are significantly younger than the hypy residue samples. This suggests that the hypy process is able to selectively remove contaminating carbon from the charcoal samples, while minimizing potential sample loss, as the maximum sample BC content is recovered via this method.

In the case of MA, the introduction of carbonaceous material with a different ^{14}C age to that of the resistant BC sample fraction appears to influence the sample ^{14}C age following standard ABA pre-treatment, although this is not apparent in the case of CHA. Hatté *et al.* (2001) suggested that during the NaOH step of the ABA pre-treatment atmospheric CO_2 dissolved into the solution might become linked with electropositive ions or incorporated directly with functional groups within the sample. They found that final acidification with HCl was not sufficient to remove this and break these ionic links, but that H_2SO_4 or ABOX-SC treatments were. The samples tested in this earlier study did not include pyrogenic carbon, and it is possible that similar trace contamination is responsible for the younger observed ^{14}C age of MA following ABA treatment. In both instances the hypy treatment appeared to remove contaminating carbon from the samples, yielding ages that are in accord with previous age measurements at several laboratories.

The ^{14}C age of the material removed by the hypy process from MA and CHA, although higher than that of the residue, is still relatively ancient (37,450 ± 750 BP and 28,050 ± 310 BP respectively). This indicates that the hypy process is removing parts of the sample matrix itself that are susceptible to contamination, leaving the inert portion unaffected. Following formation by pyrolysis, charcoal may comprise a range of carbon species which are not all in condensed aromatic form and therefore may provide sites for the adsorption of contaminating carbon. If the ABA pre-treatment does not always fully remove these sample components, this may explain the younger age of the ABA treated MA charcoal, whereas hypy does seem to selectively target contaminants. One advantage of the method in this context is that material removed in the hypy process may itself be subject to further analysis as it is retained by cryogenic trapping. These results indicate the potential of hypy as a pre-treatment technique for ^{14}C age measurement of samples with a constrained, continuous formation period. This could be extended for separation of specific carbon fractions in more complex samples, such as soil, in order to calculate aspects such as cycling and turnover of the resistant carbon fraction. Effective application of hypy for these purposes however requires more extensive investigation to establish the technique in matrices containing more thermally labile organic carbon and carbonates.

It is important to note that, for the charcoal samples tested here, environmental contamination does not appear to have introduced a significant amount of extraneous carbon with a different ^{14}C age to that of the sample. Chauvet Cave is located within the deep karst development of the Ardèche Plateau (Mocochain *et al*., 2006), therefore input from geological ^{14}C-dead carbonates to the sample during deposition is a possibility. The results from this study however support previous conclusions that if such contamination is present, it is in small amounts that do not significantly influence the overall sample ^{14}C activity (Cuzange *et al*., 2007). One possibility for the apparent absence of evidence for post-depositional environmental contamination in MA is a result of the emplacement of this sample in pyroclastic flow of poorly sorted pumicious lapilli and ash (Alloway *et al*., 2004) where processes such as organic carbon decomposition and soil carbon cycling have not provided a means for contamination. Interestingly, in the sample recovered from Holocene sediments modified by the presence of a human domestic fortified settlement (Valera, 1997), ^{14}C measurement of the untreated sample also indicates no evidence of environmental contamination, as the untreated and treated (both ABA and hypy) samples give the same age. In this instance, the ^{14}C age of the material removed during the hypy process is also indistinguishable from the treated and untreated sample ages, indicating that the amounts of contaminating material introduced during processing are very slight, and therefore insufficient to influence the age of much younger samples with high ^{14}C activity.

For the tested materials, a final hold temperature of ~550°C appears to represent the optimum conditions where non-BC material is removed, but at which degradation of the resistant sample fraction has not yet commenced. Identification of this phase is important, as it is the initial phase following removal of labile carbon sample content that is of interest in BC quantification with the hypy method, as quantification of sample BC following the onset of hydrogasification of the resistant sample fraction would lead to underestimation of the sample BC content. The conditions identified in this study for identification of this phase are in agreement with previous work on carbonaceous material (e.g. Roberts *et al*., 1995; Snape *et al*., 1989). One potential benefit of hypy is therefore the ability to provide a methodology by which uniform and standardized operating conditions can be used for isolation of BC from a wide range of materials. In chemical oxidative degradation, it is apparent that the conditions required to isolate the BC portion of specific samples vary widely depending upon the precise sample composition. For example, oxidation times to isolate kerogen and BC in sediments ranged from 10-20 hours depending upon the composition and reactivity of specific samples (Lim and Cachier, 1996). This highlights a key difficulty with isolation of the full BC component of different samples with the chemical oxidation methodology, namely of determining how resistant a sample fraction has to be to be defined chemically as BC. For example, in a recent study, Knicker *et al*., (2007) found that 12% of organic carbon derived from plant waxes (i.e. non-BC) in specific biomass samples was resistant to chemical oxidation due to hydrophobicity, rather than chemical resistance.

In hypy, the range of operating conditions required to reproducibly isolate only the chemically resistant fraction in a range of sample materials appears to be relatively constrained. Additionally, replicate analyses of MO indicate that the TOC measured in the residue after hypy treatment is highly reproducible between different runs using the same experimental conditions. Provided the sample is well homogenized prior to treatment, the reproducibility of BC determinations on a single sample by this technique appears to be very good. This indicates that a high degree of measurement precision can be achieved using the hypy method in order to consistently remove the same (non-BC) components over different runs using the same methodological protocol for a wide range of sample types.

5. Conclusions

The fact that hypy can reduce labile organic matter to volatile products in a controlled manner makes it an attractive new approach for the rapid isolation of the most resistant carbon fraction from carbonaceous samples. This suggests that hypy represents a promising new approach not only for BC quantification as an end in itself, but also for ^{14}C dating where purified BC is the target material for dating. These two goals are combined in many research studies, for example in efforts to establish the persistence and resistance of BC in the environment, and to quantify BC production rates and turnover times over extended timescales. The findings obtained here for soils and charcoal, in conjunction with the previously reported findings for lignocellulosic material, coals, and petroleum source rocks, suggest that hydropyrolysis is potentially a precise method for BC measurements in a range of sample materials. Further investigation of the applicability of hypy for these purposes should focus upon additional characterization of the hypy solid residue and products, particularly with use of spectroscopic methods, for example solid-state ^{13}C nuclear magnetic resonance, which have been useful within studies of a wide range of BC-containing matrices (e.g. Simpson and Hatcher, 2004), Further investigation of hypy applicability for ^{14}C measurement would benefit via analysis of BC materials previously shown to have suffered modern contamination. It appears that the method is potentially particularly effective for pre-treatment of samples close to the ^{14}C dating limit, where even trace contamination may be sufficient to produce a significant shift in measured sample isotopic ratio. An important additional advantage of the hypy technique is that it allows retention of the non-BC component of a sample, which may then be subject to further analysis and measurement. In applying the method to ^{14}C pre-treatment of charcoal where sample size is not limiting, it may be advantageous to select a more aggressive hypy regime, leading to some removal of the most resistant carbon fraction itself by hydrogasification to ensure complete removal of all trace contaminants. However, it is also conceivable that the method could be used for simultaneous BC quantification and sample purification for ^{14}C analysis.

Acknowledgements

Funding for this work was provided by NERC standard grant NE/C004531/1 'Charcoal Degradation in Natural Environments'. C.H. Vane publishes with permission of the Executive Director, British Geological Survey. The authors acknowledge Heléne Valladas, Bruno David and Antonio Valera for kindly providing samples of archaeological charcoal for analysis in this project, the staff of the Oxford Radiocarbon Accelerator Unit for analyses, and coordinating members of the Black Carbon ring trial (Hammes *et al*., 2007) for samples of soil standard BC reference materials.

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Figure legends

Figure 1: Schematic representation of the hypy apparatus, showing flow of high hydrogen gas pressure through the system (dashed arrows).

Figure 2: Variation of residue TOC from hypy for the reference soil samples VER (top) and BGS (bottom), showing the zone of labile C loss (A), plateau of TOC content (B) and onset of sample hydrogasification (C).

Figure 3: Weight loss (black diamonds) and residue TOC (grey squares) for the MA (Maninjau) natural charcoal sample, showing the zone of labile C loss (A), and plateau of TOC content (B). Note that for this sample, the apparent plateau at higher temperatures may represent delayed onset of hydrogasification relative to that evident in figure 2.

Figure 4: ^{14}C measurement results of the charcoal samples following no treatment, and pre-treatment with standard ABA and hypy methodologies. For samples treated by hypy both the products removed from the charcoal during treatment (product), and the BC residue following hypy were analysed. Samples are presented in order of age, where A: MA, B: CHA, and C: CAS.

Table legends

Table 1: Details of sample materials selected for hypy treatment and analysis within this study.

Table 2: TOC (%) of the BC residues following hypy treatment for samples of two reference soils (VER and BGS) and one natural charcoal (MA).

Table 3: Results of AMS ^{14}C measurements on three natural/archaeological charcoals following treatment by standard ABA methodology and hypy. For samples treated by hypy both the products removed from the charcoal during treatment (product), and the BC residue following hypy were analysed. No treatment indicates the measurement of the charcoal sample directly after extraction from deposition sediments (i.e. no laboratory treatment).