Quaternary Geochronology 4 (2009) 140–147

Contents lists available at ScienceDirect

Quaternary Geochronology

journal homepage: www.elsevier.com/locate/quageo

Research Paper

Hydropyrolysis as a new tool for radiocarbon pre-treatment and the quantification of black carbon

P.L. Ascough [a,*], M.I. Bird [a], F. Brock [b], T.F.G. Higham [b], W. Meredith [c], C.E. Snape [c], C.H. Vane [d]

[a] Department of Geography and Geoscience, University of St. Andrews, Irvine Building, St. Andrews, Fife KY16 9AL, UK
[b] Oxford Radiocarbon Accelerator Unit, Research Laboratory for Archaeology and the History of Art, Dyson Perrins Building, University of Oxford, Oxford OX1 3QY, UK
[c] School of Chemical and Environmental Engineering, University of Nottingham, Nottingham NG7 2RD, UK
[d] British Geological Survey, Kingsley Dunham Centre, Keyworth, Nottingham NG12 5GG, UK

ARTICLE INFO

Article history:
Received 23 January 2008
Received in revised form
17 October 2008
Accepted 5 November 2008
Available online 19 November 2008

Keywords:
Black carbon
Hydropyrolysis
Radiocarbon
Charcoal
Biochar

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.

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 contents 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 5–7 ky (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; BC longevity in soils appears influenced by factors such as climate, deposition environment, and land use (Czimczik and Masiello, 2007). For these reasons, 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 relies on 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.,

* Corresponding author. Tel.: +44 1334 463936; fax: +44 1334 463949.
E-mail address: pla1@st-andrews.ac.uk (P.L. Ascough).

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doi:10.1016/j.quageo.2008.11.001

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 variable, and 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 having been reported as a result of factors such as relatively high availabilities 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 also for tracer studies of environmental processes. 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 intercomparison study resulted in BC determinations from 1.1–8.0 g kg^{-1} 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. Gélinas et al., 2001).

Significant 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, as well as being able to measure the ^{14}C activity of the compounds removed by hypy. Because stereochemical rearrangements accompanying hypy are minimal due to the high pressure hydrogen, the neoformation of BC that occurs in normal thermal oxidation is suppressed, meaning that interference from formation of BC during the analytical procedure should not occur (Love et al., 1995).

In general, hypy offers a potential means to discriminate between bound and adsorbed organic species. As a result, 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 of various antiquities and in various soil matrices to assess the utility of hypy as an efficient tool for radiocarbon pre-treatment and BC quantification. 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 ± 3200–52,300 ± 2000 ^{14}C BP, and 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 contained 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 this, the ABOX-SC pre-treatment methodology was used for some