1   **Isotopes in pyrogenic carbon: a review**

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26 **Abstract**

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28   Pyrogenic carbon (PC; also known as biochar, charcoal, black carbon and soot)

29 derived from natural and anthropogenic burning plays a major, but poorly quantified, role

30 in the global carbon cycle. Isotopes provide a fundamental fingerprint of the source of PC

31 and a powerful tracer of interactions between PC and the environment. Radiocarbon and

32 stable carbon isotope techniques have been widely applied to studies of PC in aerosols,

33 soils, sediments and archaeological sequences, with the use of other isotopes currently

34 less developed. This paper reviews the current state of knowledge regarding (i)

35 techniques for isolating PC for isotope analysis, and (ii) processes controlling the carbon

36 (^{13}C and ^{14}C), nitrogen, oxygen, hydrogen and sulphur isotope composition of PC during

37 formation and after deposition. It also reviews the current and potential future

38 applications of isotope-based studies to better understanding the role of PC in the modern

39 environment and to the development of records of past environmental change.

40

41 **Introduction**

42

43   Pyrolysis accompanying the combustion of organic material under conditions of

44 restricted oxygen produces a wide spectrum of particulate, carbon-rich materials. During

45 pyrolysis carbon (C) content increases and oxygen (O) and hydrogen (H) content

46 decreases as lignocellulosic structures and other compounds degrade leading to the

47 formation of chemically stable aromatic rings. As pyrolysis temperatures increase these

48 aromatic rings coalesce into polyaromatic configurations, and increasingly form ordered

49 microcrystalline domains, conferring even higher chemical stability (Goldberg, 1985;

50 Eckmeier et al., 2007). The resulting material therefore appears highly resistant to post-

51 depositional alteration, particularly in anoxic environments (e.g. Masiello, 2004;

52 Czimczik et al., 2005; Preston and Schmidt, 2006).

53   This material is known by a variety of names including charcoal, micro-charcoal,

54 carbonaceous spherules, soot, fusain, elemental carbon, oxidation resistant elemental

55 carbon, microcrystalline graphite, black carbon and graphitic black carbon (Preston and

56 Schmidt, 2006; Bird, 2006). The range of names used to describe this material reflects not

57 only its compositional complexity but also its importance across a range of disciplines,

58 each of which has evolved not only a terminology but also a set of methodologies for the

59 analysis of this material and interpretation of the results. Recently, the term 'biochar' has

60 been added to the lexicon (Karaosmanoglu et al., 2000), and has come to refer to

61 pyrogenic carbon produced purposefully by humans under controlled pyrolysis conditions

62 in order to generate (i) gases for power generation (syngas), (ii) a range of bio-oils, and

63 (iii) biochar for use as a soil ameliorant in agriculture and for carbon sequestration (e.g.

64 Lehmann et al., 2006).

65   Pyrogenic carbon (PC) is used here to denote carbon-rich material of any kind

66 produced by partial combustion or pyrolysis, either naturally or anthropogenically. An

67 important conceptual development has been the recognition that PC represents a

68 'combustion continuum' (e.g. Hedges et al., 2000; Masiello, 2004). At the low

69 temperature end of this continuum lies slightly charred biomass, of low aromaticity, high

70 reactivity, whereas at the other end lies black carbon particles and a range of individual

71 pyrogenic molecules, with high aromaticity and low reactivity, formed in part from gas

72 phase condensation at high temperature. The existence of this continuum means that PC

73 is likely to exhibit a range in the degree to which it will interact with its environment after

74 formation and the degree to which it is resistant to physical or chemical degradation after

75 formation (Figure 1).

76   PC of natural and anthropogenic origin is a common minor component of many

77 environments and materials and is significant because of its potentially high resistance to

78 decay, which may result in extended environmental persistence. As a result, PC is present

79 in rocks as old as Devonian (362-365 Ma; Cressler, 2001), coal measures (Scott and

80 Glasspool, 2007; Scott, 2009), soils (Schmidt et al., 2002; Lehmann et al., 2008), aerosols

81 (Cachier et al., 1989; Gustaffsson et al., 2009) as well as terrestrial and marine sediments

82 (Bird and Cali, 1998; Masiello and Druffel, 1998) and terrestrial (Manino and Harvey,

83 2004; Hockaday et al., 2007) and marine waters (Manino and Harvey, 2004; Dittmar and

84 Koch, 2006; Dittmar and Paeng, 2009).

85   As with all matter, PC is composed of a range of major and minor isotopes, the

86 concentration of which reflect a complex mix of processes associated with the source of

87 each element in the material, plus the processes by which, and the conditions under

88 which, each element was incorporated into the material. Post-formation, modification of

89 the isotope composition of the material can occur by a range of interactions with the

90 environment, and in some cases by radioactive decay. The major component of PC is

91 carbon, which has two stable isotopes; the major isotope carbon-12 (^{12}C) and the minor

92 isotope carbon-13 (^{13}C), measured as a ratio ($^{13}C/^{12}C$) and expressed in delta notation

93 ($\delta^{13}C$), as parts per thousand (per mil; ‰) deviations from the known composition of a

94 standard. Carbon also has a radioactive isotope, carbon-14 (^{14}C), and this forms the basis

95 of radiocarbon dating which is applicable to samples with ages up to c.50,000 years

96 before present. In addition, PC contains minor elements that also have a number of

97 isotopes, including nitrogen ($^{15}N/^{14}N$; $\delta^{15}N$), oxygen ($^{18}O/^{16}O$; $\delta^{18}O$), hydrogen ($^{2}H/^{1}H$;

98 δD) and sulphur ($^{36}S/^{34}S$; $\delta^{34}S$). Although these elements often comprise a relatively

99 minor proportion of PC, and hence are likely to present analytical challenges, the

100 abundance of all these isotopes encodes information on the origin, formation and/or post-

101 formation history of PC.

102   The carbon isotope composition of PC is particularly significant, as it has been

103 widely applied across a range of disciplines for obtaining environmental and

104 palaeoenvironmental information, assisting in source apportionment and providing

105 chronologies for sedimentary and archaeological deposits. It is the purpose of this paper

106 to review the current state of knowledge of the many factors controlling the carbon

107 isotope composition of PC, and the potential for other isotopes of PC to contribute to the

108 this knowledge in future.

109

110 **The carbon isotope composition of unpyrolysed biomass**

111

112   *Photosynthesis and environment*

113   The $\delta^{13}C$ value of PC is controlled most fundamentally by the $\delta^{13}C$ value of the

114 organic material that was pyrolysed. While biochar can be made from unusual feedstocks

115 such as algae, the vast majority of PC is derived from terrestrial biomass.

116   The carbon isotopic composition of terrestrial plants varies from about –8 to –34‰

117 (Bender, 1971). The most significant differences derive from markedly different

118 magnitudes of isotope fractionation during photosynthesis following one of three

119   pathways (C_3, C_4 and CAM; e.g. Farquhar et al., 1980; Hatch, 1987; Sage, 2004). Most

120   plants use the more ^{13}C-discriminating C_3 pathway, leading to low δ^{13}C values (trees,

121   shrubs, forbs, lianas, and temperate grasses; mean δ^{13}C = -27‰). Plants using the less

122   ^{13}C-discriminating C_4 pathway include most tropical grasses and many forbs, and have

123   higher δ^{13}C values (mean δ^{13}C = -13‰). Plants using crassulacean acid metabolism

124   (CAM plants) are uncommon except in arid regions, and can fix atmospheric carbon

125   either via ribulose biphosphate carboxylase (i.e. C_3 pathway) or via a C_4-like sequence

126   utilising carboxylation and reduction of phosphoenolpyruvate, resulting in a range of δ^{13}C

127   values intermediate between C_3 and C_4 plants (Osmond et al., 1973; O'Leary, 1981)

128   The δ^{13}C values of C_3 biomass are generally in the range –25 to –32‰. Variations

129   of several per mil within this range are controlled by factors such as species (Ehleringer

130   et al., 1987), latitude/altitude (Körner et al. 1991; Bird et al., 1994; 1996), soil water

131   deficit (Stewart et al., 1995), irradiance (Ehleringer et al., 1986; 1987) topographic

132   position (Balesdent et al., 1993) and the degree of re-utilization of respired CO_2 (Van der

133   Merwe and Medina, 1989; Broadmeadows et al., 1992). Within the C_4 photosynthetic

134   pathway, variations in δ^{13}C can be primarily attributed to availability of water and light

135   (Buchmann et al., 1996; Ehleringer, 1993).

136   *Other effects*

137   In addition to pathway- and environment-specific isotope effects, the various parts

138   of any individual plant (roots, stems, leaves) and the various compounds that make up the

139   different tissue types within a single plant can vary by several per mil due to differing

140   fractionations associated with biosynthetic pathways leading to the formation of different

141   compounds (e.g. Leavitt and Long, 1986; Brugnoli and Farquhar, 2000; Benner et al,

142   1987). For example, the major components of wood (i.e. cellulose and lignin) differ by 4-

143   7‰, with cellulose enriched by 1-2‰ in ^{13}C relative to whole tissue and lignin depleted

144   by 2-6‰ compared to whole tissue (Benner et al., 1987).

145   Since industrialization, the δ^{13}C value of the atmosphere has decreased by

146   approximately 1.5‰, due to the addition of CO_2 derived from fossil fuel burning (Friedli

147   et al., 1986) and this gradual decline must also have been manifest in all photosynthetic

148   tissue formed over this period. On longer timescales, it is also thought that the δ^{13}C value

149   of the atmosphere during the last ice age was 0.3‰ (Leuenberger et al., 1992) to ~1‰

150   lower than the pre-industrial atmospheric $\delta^{13}C$ value (Marino et al., 1992), and this

151   difference would be directly reflected in plants growing at that time.

152   *Radiocarbon*

153   In contrast to the stable isotopes of carbon, ^{14}C is an unstable isotope that decays by

154   β-emission with a half-life of 5730 years (Godwin, 1962), produced cosmogenically in

155   the atmosphere by absorption of thermal neutrons by ^{14}N. ^{14}C is rapidly oxidized to $^{14}CO_2$

156   and distributed throughout the biospheric C reservoir, where the global $^{14}C/^{12}C$ ratio is

157   c.10^{-12} (Levin and Hesshaimer, 2000; Stuiver and Braziunas, 1993). Constant production

158   and rapid global atmospheric mixing make ^{14}C highly suitable for absolute dating,

159   although measurement is limited to samples younger than c.50 ky BP (Godwin, 1962).

160   PC forms one of the most common materials submitted for ^{14}C dating (Bird, 2006) due to

161   its high C content and environmental longevity, with the further advantage that plant-

162   derived PC is largely in equilibrium with the atmospheric C reservoir and is thus not

163   subject to any reservoir-dependant ^{14}C age offsets (e.g. Stuiver and Polach, 1977).

164   As ^{14}C age is based upon measured $^{14}C/^{12}C$ (or $^{14}C/^{13}C$) ratios, all measurements are

165   normalized relative to $\delta^{13}C = -25‰$ with respect to VPDB (Donahue et al., 1990). This

166   accounts for kinetic isotope fractionation effects upon ^{14}C age, meaning the sample ^{14}C

167   age is dependant solely upon i) the time since final exchange with exogenous C (as a

168   function of radioactive decay), and ii) the sample ^{14}C content at this point. It is therefore

169   key that the sample C content corresponds solely to the event of interest for dating. In

170   addition to issues of exogenous C contamination and post-depositional

171   disturbance/mixing, the ^{14}C age of PC derived from long-lived plant species can be

172   greatly in excess of the date of plant death. This 'old wood' effect is exacerbated at

173   archaeological sites by activities such as the use of driftwood as a fuel source, meaning

174   the use of charcoal from short-lived species or samples with identifiable final growth

175   structures is advocated (Facorellis and Maniatis, 1998; Reimer et al., 2002; Ascough et

176   al., 2005). Interpretation is also complicated by atmospheric ^{14}C activity fluctuations

177   ($\Delta^{14}C_{atm}$). Release of radiocarbon-dead fossil fuel CO_2 in the past c.200 years has reduced

178    $\Delta^{14}Catm$ (Suess, 1955). As the magnitude of this $\Delta^{14}C_{atm}$ is unknown, accurate correction

179   is difficult, increasing the age uncertainties in samples of this age (Stuiver, 1978;

180   McCormac et al., 1998).

181   Additionally, atmospheric detonation of nuclear weapons from the early 1950's

182   generated an estimated 630×10^{26} ^{14}C atoms (known as the 'bomb spike'), sharply

183   elevating $\Delta^{14}C_{atm}$ (Hesshaimer et al., 1994; Levin and Kromer, 1997; Levin and

184   Hesshaimer, 2000). Although this effectively precludes the use of traditional ^{14}C age

185   measurement in affected samples, the bomb spike and subsequent $\Delta^{14}C_{atm}$ decline

186   (following the 1962 Nuclear Test Ban Treaty) allows high annual chronological

187   resolution and transient tracing of global carbon transfer processes (e.g. Leifeld, 2008).

188

189   **Modification of carbon isotope composition during pyrolysis**

190

191   δ^{13}C measurements of PC are used as palaeoenvironmental proxy to reconstruct climatic

192   conditions and vegetation distribution (e.g. Clark et al., 2001; Pessenda et al., 2005;

193   Ferrio et al., 2005; Hall et al., 2008; Aguilera et al., 2009). Such analyses include both

194   bulk material containing charcoal C and isolated charcoal fragments, where the latter

195   reduces complexity if bulk samples comprise multiple, isotopically distinct components.

196   One potential complication is isotope fractionation during charcoal formation. If such

197   fractionation is extant, a correction factor could be used to account for the effect (e.g.

198   Turney et al., 2006; Werts and Jahren 2007). However this approach would only be valid

199   if pyrolysis-induced isotope fractionation were of a universal magnitude between

200   samples. This is relevant given evidence that δ^{13}C discrimination between the original

201   plant material and charcoal ($\Delta^{13}C_{Char}$) varies between samples. To illustrate this a

202   compilation of published results of pyrolysis impact on isotope values for different

203   materials is provided in Table 1. These indicate $\Delta^{13}C_{Char}$ increases with pyrolysis

204   temperature by up to ~2‰ (Ferrio et al., 2006; Turney et al, 2006; Ascough et al., 2008a;

205   Das et al., 2010). Initial $\Delta^{13}C_{Char}$ increases are attributed to loss of isotopically lighter

206   extractives from >100°C and/or 'trapping' of isotopically heavier cellulose-derived

207   carbon within the initial charcoal structure (Jones et al., 1993; Czimcizk et al., 2002;

208   Poole et al., 2002; Hakkou et al., 2006). Subsequent $\Delta^{13}C_{Char}$ decreases of 1-2‰ in

209   charcoal and biomass burning aerosols at >300°C (Ascough et al., 2008a; Czimczik et al.,

210   2002; Turney et al., 2006; Jones et al., 1993; Bird and Gröcke, 1997; Jones and Chaloner

211   1991) are generally attributed to preferential loss of less thermally stable and isotopically

212 heavier cellulose (Maunu., 2002; DeNiro and Hastorf, 1985; Cachier et al., 1985; Benner

213 et al., 1987; Loader et al., 2003; Williams and Besler, 1996; Xiao et al., 2001). Above

214 ~400°C polyaromatization dominates and it has been suggested that ^{13}C may be

215 preferentially lost during C=C bond formation, raising the possibility of further δ^{13}C

216 depletion (Qian et al., 1992; Krull et al., 2003).

217   Along with temperature, there is evidence $\Delta^{13}C_{Char}$ is modulated by

218 starting material and pyrolysis conditions. This may result from differences in the

219 proportion of isotopically distinct volatile and refractory compounds between plants, δ^{13}C

220 offsets between the same components in different plants, or differences in the proportions

221 of isotopically distinct components diverted to, or retained within the charcoal structure

222 (Turekian et al., 1998; Krull et al., 2003; Ascough et al., 2008a). $\Delta^{13}C_{Char}$ values also

223 appear larger in solid charcoal, aerosol particles, n-alkanes, polycyclic aromatic

224 hydrocarbons (PAH), and CO_2 produced from pyrolysis and combustion of C_4 plants

225 compared to C_3 plants (Collister et al. (1994; Cachier et al., 1985; O'Malley et al., 1997;

226 Ballentine et al., 1996; 1998; Turekian et al., 1998; Krull et al., 2003; Das et al., 2010).

227   Duration of charring does not induce significant $\Delta^{13}C_{Char}$ differences

228 (Turney et al., 2006; Ascough et al., 2008a; Das et al., 2010), however the proportion of

229 oxygen present during pyrolysis may modulate $\Delta^{13}C_{Char}$. Significant δ^{13}C offsets between

230 charcoal produced under vacuum versus open fires have been attributed to accelerated

231 loss of ^{13}C-depleted cellulose during pyrolysis under vacuum versus 'natural' conditions

232 in the presence of oxygen (Leavitt et al., 1982; Turney et al., 2006; Krull et al., 2003).

233 There is also evidence that various factors influencing $\Delta^{13}C_{Char}$ operate in conjunction, for

234 example, in an investigation integrating stable isotope analysis with solid state ^{13}C

235 nuclear magnetic resonance, Ascough et al (2008a) found pyrolysis atmosphere did not

236 influence softwood $\Delta^{13}C_{Char}$, but did influence $\Delta^{13}C_{Char}$ in hardwood.

237   Key points therefore include consideration as to whether laboratory-charring

238 experiments replicate the $\Delta^{13}C_{Char}$ observed under 'natural' burning events. The

239 variability in $\Delta^{13}C_{Char}$ complicates prediction of charcoal δ^{13}C on either a linear or mass-

240 balance basis, making precise $\Delta^{13}C_{Char}$ correction difficult. However, in homogeneously

241 pyrolysed samples the relative intra- and inter-sample δ^{13}C differences appear preserved.

242 In addition, data in Table 1 suggest that in the majority of instances $\Delta^{13}C_{Char}$ is on the

243   order of 1-2‰. Larger values are identified in some studies, however it is important to

244   note that these extreme values could result from specific pyrolysis conditions and

245   particular care should be taken during interpretation of such data. Therefore

246   palaeoclimatic reconstruction and C_3 versus C_4 source apportionment is possible using

247   charcoal $\delta^{13}C$ measurements, provided appropriate error terms are used to account for any

248   variation in $\Delta^{13}C_{Char}$ between samples (e.g. Turekian et al., 1998; Cachier et al., 1985;

249   Van-Klinken et al. 1994; Vernet et al. 1996; February 2000; Ferrio et al., 2006; Pessenda

250   et al., 2005; Hall et al., 2008).

251

252   **Post-formation alteration of the carbon isotope composition of pyrogenic carbon**

253

254   *Chemical alteration*

255   PC is often considered to be highly resistant to post-depositional alteration (e.g.

256   Czimczik et al., 2005; Preston and Schmidt, 2006). However this assumption is

257   challenged by evidence suggesting alteration and degradation of charcoal in a range of

258   environmental deposits. This appears to involve oxidative "weathering", with addition of

259   oxygen to the charcoal aromatic skeleton, and an increase in carboxylic (COOH and

260   COO-) groups (Cohen-Ofri et al., 2006; Ascough et al., 2010a). Extreme effects of

261   degradation upon apparent charcoal abundance, resulting in near complete loss of

262   charcoal from some archaeological deposits over millennia, have also been reported (Bird

263   et al., 2002). In addition, a number of comparative mass balance studies have

264   demonstrated significant loss of PC from on decadal to millenial timescales (Bird et al.,

265   1999; Hammes, et al., 2008a; Kuzyakov et al., 2009) but not on annual timescales (Major

266   et al., 2009; Eckmeier et al., 2007).

267   A key concern for the stable isotope analysis of PC is the potential for post-

268   depositional addition of exogenous material, or loss of isotopically distinct indigenous

269   carbon. Either could compromise the interpretation of stable isotopes in PC as a proxy

270   climatic record or modify the apparent proportion of PC derived from a particular source.

271   The degree to which this might occur is likely to be controlled by the conditions of

272   formation of the PC and the chemistry of its environment of deposition. For example, it is

273   clear in some charcoal formed at lower temperatures a proportion of (isotopically

274   heavier) cellulosic C may not be completely thermally-degraded (Ascough et al., 2008a).

275   This component may then be subject to degradation and removal via abiotic or

276   microbially-mediated processes (DeNiro and Hastorf, 1985; Ascough et al., 2010b).

277   These processes appear mediated by chemistry of the depositional matrix, and

278   Figure 2 shows the effect on $\delta^{13}C$ of exposure of Sugarcane bagasse (C_4) biochar

279   produced at a range of temperatures and emplaced beneath leaf litter on the surface of a

280   rainforest (C_3) soil. Changes in $\delta^{13}C$ by three months were negligible except for the

281   lowest temperature (310˚C) biochar exposed under conditions of elevated pH. This

282   suggests that pH may play a significant role in mediating the interactions between PC and

283   its local environment, as has previously been suggested by Braadbaart et al. (2009).

284   For PC in pure C_3 temperate and forest environments any changes in $\delta^{13}C$ resulting

285   from interactions with the local environment are likely to be small due to similarity in

286   $\delta^{13}C$ between PC and organic carbon from a local (also C_3) source. In addition,

287   interpretation of $\delta^{13}C$ variations in PC from archaeological sequences has been attempted

288   with some success (Hall et al., 2008).

289   *Physical effects*

290   The issue of interpreting $\delta^{13}C$ of PC in mixed C_3/C_4 regions such as tropical

291   woodlands and savannas is complicated by several factors. It is likely that physical

292   fractionation of PC occurs during combustion, with the residue of burning on site biased

293   towards larger wood-derived PC with the C_4-derived PC exported to a greater degree as

294   fine particulates from the same site. Further sorting by size, thereby altering $\delta^{13}C$ value is

295   likely during later transport of PC by water (Major et al., 2009) and wind (Bird and Cali,

296   1998) to a site of deposition. In addition, it is possible that C_3 and C_4-derived PC may

297   well degrade at different rates owing to different particle sizes and potentially different

298   conditions of formation. There is as yet little experimental work in this area (Das et al.,

299   2010), but the likelihood that there will be significant changes in $\delta^{13}C$ in mixed C_3/C_4 PC

300   arising from both physical and chemical processes suggests interpretation should be

301   approached with caution.

302   *Radiocarbon*

303   In the case of radiocarbon, even trace contamination by exogenous carbon of either

304   younger or older age can lead to erroneous dates for PC (Gillespie et al., 1997; Bird et al.,

305   1999; Alon et al., 2002), and therefore to erroneous chronologies for sedimentary and

306   archaeological sequences. As with stable isotopes, the degree to which PC will be

307   contaminated by exogenous carbon likely depends on the characteristics of the PC itself,

308   its environment of deposition and time of exposure to the environment. An example from

309   an ongoing experiment where radiocarbon dead wood was pyrolysed at 450°C and

310   emplaced for three months under litter with and without limestone in a tropical forest is

311   shown in Figure 3. It can be seen that while there has been negligible ingress of young

312   carbon from the litter only treatment, there has been measureable ingress of modern

313   carbon in the litter plus limestone treatment, and that this contamination (equivalent in

314   age terms to >1,000 years at 50,000 yrs BP) is not removed by conventional pretreatment

315   prior to dating. This again implies that pH exerts significant control on interactions

316   between PC and its environment, as suggested by Braadbaart et al. (2009).

317

318   **Isolation and quantification of pyrogenic carbon for isotope analysis**

319

320   A number of techniques have been applied to determining the abundance of PC in a

321   range of sample matrices (see Schmidt et al., 2001; Masiello, 2004; Hammes et al., 2007;

322   for reviews), but not all of these isolate PC, or a component of PC, that can be further

323   analysed for isotope composition. Of those techniques that do aim to isolate PC, or a

324   component of PC, most have been used to determine carbon isotope composition.

325   Chemothermal oxidation (CTO-375) involves acid pre-treatment followed by oxidation

326   of the organic component of a sample at 375°C for 18 hours (Elmquist et al., 2004). This

327   technique has been successfully employed to determine the $\delta^{13}C$ value of PC in aerosol

328   samples (Zencak et al., 2007), and as a radiocarbon pretreatment technique for PC by

329   being able to apportion Asian aerosolic 'brown haze' between fossil fuel and biomass

330   burning-derived PC (Gustaffsson et al., 2009).

331   The acid dichromate oxidation techniques seek to oxidize organic carbon at a faster

332   rate that PC, thereby isolating a component known as OREC (Oxidation Resistant

333   Elemental Carbon; Bird and Grocke, 1997). This technique has been used to determine

334   the $\delta^{13}C$ value of OREC in soils (Wynn and Bird, 2007), marine sediments (Bird and

335   Cali, 1998) and archaeological sediments (Bird et al., 2002). This is an aggressive

336   technique with PC yield strongly dependant on oxidation temperature and time, and more

337   recent work has demonstrated that other components (e.g. waxes) can survive oxidation

338   (Knicker et al., 2007; Ascough et al., 2010c).

339   A biomarker approach to isolation of PC involves oxidation with nitric acid,

340   followed by isolation and quantification of a range of benzene polycarboxylic acids

341   (BPCA's) released specifically from oxidation of PC in a sample (Brodowski et al.,

342   2005). This treatment leads to the quantification of a number of PC-derived components

343   all of which are potentially amenable to carbon isotope determination and/or radiocarbon

344   dating, as has also been achieved for free polycyclic aromatic hydrocarbons from aerosols

345   and (Sheesley et al., 2009) and sediments (Kanke et al., 2004).

346   A recently developed alternative technique is the use of catalytic addition of

347   hydrogen to reductively separate labile and refractory PC components. This is achieved

348   via pyrolysis under high H_2 gas pressures, known as hydrogen pyrolysis (hypy) (Roberts

349   et al., 1995). Hypy results in total reductive conversion and removal of common PC

350   contaminants, such as cellulose and humic substances, isolating a chemically consistent,

351   highly aromatic component within isolated PC fragments, and complex matrices such as

352   soils (Ascough et al., 2008b; Ascough et al., 2010c). Advantages of this approach also

353   include suppression of the PC neoformation that complicates analysis using normal

354   thermal oxidation techniques (Love *et al*., 1995, Brocks *et al*., 2003). Hypy also

355   facilitates characterization of different sample components, for example, enabling

356   comparison of polyaromatic domain size between samples, with the potential to use such

357   measurements in assessment of post-depositional diagenesis of the PC aromatic structure

358   (Ascough et al., 2010c).

359

360   **Pre-treatment of pyrogenic carbon for radiocarbon dating**

361   As isotope fractionation of ^{14}C is corrected by measurement of $\delta^{13}C$ value, isolation

362   of PC for radiocarbon analysis tends to be more concerned with ensuring complete

363   removal of contaminants rather than quantitative isolation. This is because even trace

364   contamination by carbon of a different age will compromise the reliability of a

365   radiocarbon measurement on a sample. Contamination can occur via a number of routes.

366   Some PC has a large internal and external surface area and acts as a sorbant for a range of

367 organic and inorganic compounds, with 'activated' carbon being an extreme example

368 (Gustaffsson et al., 2001).

369   During what is often millennia between the formation of charcoal and its sampling

370 for analysis, PC in the natural environment will have been exposed to soil solutions

371 containing a range of organic compounds and some, including carbohydrates, amino

372 acids and phenolics, have been shown to adsorb readily to natural PC (Pietikäinen et al.

373 2000). In addition, PC often forms a suitable substrate for microbial colonization and

374 several studies have demonstrated enhanced soil microbial activity associated with

375 charcoal (e.g. Zackrisson et al., 1996). Finally, combustion of organic matter leaves a

376 residue of ash, the main component of which is commonly CaO (lime) and over time this

377 can become converted to carbonate, potentially introducing further contamination into the

378 charcoal structure (Demeyer et al., 2001).

379   Routine pre-treatment for radiocarbon dating involves washing sequentially with

380 acid for sediment carbonate removal, followed by alkali to extract organic contaminants

381 (including humic acids), and a final acid wash to remove any atmospheric CO_2 absorbed

382 in the base step (ABA or AAA pre-treatment; Table 2). This technique is relatively rapid,

383 and appears to provide robust results for a large number of samples. However, retention

384 and analysis of material removed into solution during ABA treatment may be impractical,

385 and in many instances the alkali step may result in virtually complete dissolution of

386 charred samples (Hedges et al., 1989; Rebollo et al., 2008).

387   Several studies have shown that the ABA technique does not always remove all

388 contaminating carbon (e.g. Goh, 1979; Gillespie et al., 1992; Harkness et al., 1994;

389 Chappell et al., 1996; Higham et al., 1998). Such issues become critical with increasing

390 sample ^{14}C age, when even small quantities of exogenous carbon can have a significant

391 impact upon the measured sample ^{14}C activity, and in some ancient charcoal samples

392 ABA pre-treatment results in erroneously young ages (e.g. Higham et al., 2009a).

393 Unfortunately the age range for which sample contamination issues is particularly acute

394 (~30-40ka BP), also relates to a timeframe of key prehistoric chronologies, such as the

395 spread of modern humans in Australia and western Eurasia.

396   Bird et al., (1999) described an alternative pre-treatment technique, involving a

397 more aggressive and exhaustive removal of labile carbon. In this, the final acid wash of

398 the ABA treatment is replaced with an oxidation step in acidified potassium dichromate

399 ($K_2Cr_2O_7$ in H_2SO_4) to isolate the most resistant, highly-aromatic fraction of the sample

400 (Bird and Gröcke, 1997). This is followed by stepped combustion (typically at 300°C,

401 600°C and 900°C), to remove any final traces of labile C (Table 2). The Acid-Base-

402 Oxidation-Stepped Combustion (ABOX-SC) method appears effective in removing

403 contamination from older samples, resulting in charcoal ^{14}C ages that are more consistent

404 with complementary dating evidence than the ABA method (Turney et al., 2001; Bird et

405 al., 2003; Higham et al., 2009a, 2009b). However, the rigorous ABOX-SC pre-treatment

406 is very harsh, and results in large losses of sample material. In this regard, the hypy

407 technique offers advantages as a ^{14}C pre-treatment, as it is possible to effectively degrade

408 compound classes routinely targeted for removal without unnecessary loss of the resistant

409 PC component of interest for dating, minimizing sample loss (Ascough et al., 2008b). In

410 addition, where sample size is limiting, oxygen plasma ashing has demonstrated potential

411 as a controllable 'light touch' pre-treatment technique (Bird et al., in press).

412

413 **Applications of carbon isotopes in pyrogenic carbon**

414

415 The use of carbon isotopes in pyrogenic carbon has a long history. A bread roll

416 pyrolised by the volcanic eruption of Pompeii in AD79 was one of the first samples to be

417 radiocarbon dated, and the radiocarbon date obtained on the sample was within error of

418 the known age of the eruption (Arnold and Libby, 1949). The use of radiocarbon dating

419 as a geochronological tool is now commonplace with thousands of dates on pyrogenic

420 carbon produced every year (Bird, 2006). The correction of radiocarbon activity using

421 δ^{13}C of the sample is required for all radiocarbon dates, but the application of stable

422 isotopes in pyrogenic carbon as an end in itself is an innovation of the last few decades

423 (e.g. February and van der Merve, 1992).

424 Carbon isotopes are used to fingerprint carbon sources and elucidate processes

425 involving pyrogenic carbon across a wide range of disciplines and in a wide range of

426 sample matrices. In palaeoenvironmental reconstruction and archaeology the δ^{13}C value

427 of pyrogenic carbon has been used at scales ranging from the inference of

428 palaeoenvironments surrounding human occupation sites in the late Pleistocene using

429   macro-charcoal $\delta^{13}C$ value (Hall et al., 2008) to glacial-interglacial changes in biomass

430   burning regime and vegetation across the Sahel using fine PC isolated from marine

431   sedimentary sequences (Bird and Cali, 1998). Further, temporal sequences of $\delta^{13}C$

432   derived from charred grains in archaeological sediments have been used to reconstruct

433   climate-derived aridity variations, and provide an assessment of early agricultural

434   practices such as irrigation (Ferrio et al., 2005, 2006; Araus and Buxó 1993; Araus et al.

435   1997, 1999).

436   The degree to which the $\delta^{13}C$ value of natural PC can currently be interpreted as an

437   environmental indicator is hampered by a poor understanding of the processes leading to

438   physical fractionation of C_3 and C_4 derived pyrogenic carbon during burning (Das et al.,

439   2010) and during transport to a site of deposition. Where the PC can be assumed to have

440   been derived from a C_3-only source low $\delta^{13}C$ values can be generally interpreted as

441   indicating environments of closed forest high water availability and a high degree of re-

442   utilization of respired CO_2, with high $\delta^{13}C$ values interpreted as indicative of more open

443   forest with a low degree of reutilization of respired CO_2 and water limitation of primary

444   production.

445   In studies of PC in the modern environment, radiocarbon has been used to

446   demonstrate the longevity of pyrogenic carbon in the terrestrial soils and sediments prior

447   to ultimate burial in ocean sediments (Masiello and Druffel, 1998). In addition, both

448   radiocarbon and $\delta^{13}C$ value have been used to discriminate between potential sources of

449   pyrogenic carbon in aerosols (Glaser et al., 2005; Gustaffsson et al., 2009), sediments

450   (Masiello and Druffel, 2003) and soils (e.g. Bird et al., 1999; Gouveia et al., 2002;

451   Schmidt et al., 2002; Bird et al., 2002).

452   Kuzyakov et al. (2009) in the case of radiocarbon and Steinbeiss et al. (2009) in the

453   case of $\delta^{13}C$ have already demonstrated the potential of artificial isotope labelling to

454   investigate PC degradation and elucidate PC-soil interactions. The preliminary results

455   presented in Figures 2 and 3 further suggest that both radiocarbon and $\delta^{13}C$ also have

456   considerable unexploited potential as a natural tracer for the study of PC degradation and

457   interactions between PC and its environment.

458

459   **Other stable isotopes in pyrogenic carbon**

460

461   There has been little research into the systematics of other isotopes present in PC,

462   partly because (i) these are present in only low concentrations in lignocellulose-derived

463   PC, (ii) the processes controlling isotope fractionation during pyrolysis are not well-

464   understood and (iii) it is likely that a significant proportion of at least O, N and H in PC is

465   either exchangeable, or may be subject to overprinting by exogenous components after

466   formation. However, there is potential for progress in the application of other isotope

467   systems for obtaining palaeoenvironmental/archaeological information, insights into the

468   conditions of formation, and also on post-formation interactions between PC and its

469   environment.

470   *Nitrogen isotopes*

471   Further potential exists in using the nitrogen isotopes to examine the dynamic

472   interactions between biochar and its environment, as some biochar feedstocks, such as

473   manures and algae are high in nitrogen. Such studies can include the incorporation of

474   natural or artificial isotope tracers to enable assessment of the bioavailability of biochar

475   nitrogen and interactions between fertilizers, plants and biochar (e.g. Tagoe et al., 2008;

476   Rondon et al., 1996).

477   Measurement of $\delta^{15}N$ in carbonized plant seeds from archaeological sites has

478   been employed to assess prehistoric soil fertility and management practices (Araus et al.,

479   2007; Aguilera et al., 2008). However there is limited research concerning the potential

480   for nitrogen isotope fractionation during charcoal formation. In cereal grains charred at

481   temperatures up to 300°C, Bogaard et al., (2007) and Aguileria et al., (2008) report no

482   significant changes in isotope composition, suggesting that the original environmental

483   signal is preserved. However Turekian et al., (1998) found $\delta^{15}N$ enrichment in aerosol

484   particulates and ash of +6.6‰ and +2.5‰ respectively, during laboratory C_3 vegetation

485   burns at up to 225°C.

486   Variable $\delta^{15}N$ fractionation has also been observed in charcoal during

487   production, attributed to accessing of isotopically distinct N pools (comprising free

488   ammonia, free and bound amino acids) at different temperatures. Analysis of $\delta^{15}N$ in

489   charcoal prepared from wood of *Pinus sylvestris* and *Rizophora apiculata* by laboratory

490   charring under N_2 between 300-600°C (Table 2) shows no clear relationship between

491    $\delta^{15}N$ and production conditions, although the values of softwood (*Pinus. sp*) charcoal

492    $\delta^{15}N$ are slightly higher overall than in hardwood (*Rizophora sp.*). Treatment of selected

493   samples with 1M NaOH results in $\delta^{15}N$ changes of between +4.37‰ and -1.63‰,

494   suggesting caution should be used in interpretation of charcoal $\delta^{15}N$ in samples subjected

495   to alkali laboratory treatment, or which have been exposed to changing pH conditions

496   during deposition. A further important point is that the low N% of charcoal samples

497   (typically <1%) may mean a higher level of uncertainty (e.g. ±0.8% at 1σ), exceeding the

498   precision on internal standards for $\delta^{15}N$, are inevitable for $\delta^{15}N$ measurements of PC

499   samples.

500   *Oxygen and hydrogen isotopes isotopes*

501   Newly-formed charcoal contains a significant proportion of oxygen and hydrogen,

502   and O/C ratio increases over time upon environmental exposure through oxidation of the

503   PC surface (Cheng et al., 2006; 2008). Therefore the potential exists to use $\delta^{18}O$ and δD

504   to obtain information on environment and/or conditions of formation and/or the dynamics

505   of PC degradation, but there have as yet been no studies in this area. Interpreting oxygen

506   and hydrogen isotope data from PC is likely to be a challenge in the light of multiple

507   controls on isotope composition and issues of likely exchangeability of at least a

508   proportion of hydrogen in PC.

509   *Sulphur isotopes*

510   Sulphur isotopes mainly encode information relating to sulphur source(s) (Peterson

511   and Fry, 1987) and hence may be of use in discriminating PC sources in aerosols and

512   archaeological charcoal as well as providing a tracer that might also be of use in tracking

513   interactions between PC and the soil environment. However, there are as yet no published

514   studies of sulphur isotopes in PC.

515

516   **Conclusions**

517   The analysis of carbon isotopes in PC has already greatly enhanced our

518   understanding of the role of pyrogenic carbon in the earth system. Some techniques, such

519   as radiocarbon dating of charcoal are well established and have played a pivotal role in

520   developing robust chronologies for environmental change and the development of human

521   societies. The major challenges for future research on PC remain the further development

522 and refinement of techniques that can reliably isolate and decontaminate one or more

523 components PC for further analysis, including isotope analysis. There remain significant

524 issues of inter-comparability between results derived using different techniques and

525 indeed different laboratories using the same techniques. Hydrogen pyrolysis, and

526 biomarker-based approaches represent comparatively new developments that may assist

527 in establishing agreed benchmark protocols for PC isolation for isotope analysis, as

528 opposed to simply the determination of PC abundance.

529 　　　Isotope-based tracer studies will be key to arriving at a predictive, process-based

530 understanding of the origin, behaviour and longevity of PC in a range of environments

531 from terrestrial to marine. Equally, isotope analysis of PC has considerable unexploited

532 potential for the development of records of past environmental change. New

533 opportunities for isotope-based studies are emerging in biochar research where key

534 questions surround the dynamics of PC interactions with the soil-plant system under a

535 range of environmental drivers.

536 　　　The analysis of isotopes other than carbon in PC is in its infancy. While there are

537 significant opportunities to undertake multi-isotope tracer studies of PC, initial research

538 must focus on development of a basic understanding of the primary determinants of N, O,

539 H and S isotope composition in PC. This must include determining the degree to which O

540 and H isotopes in particular are readily exchangeable, as this might limit the degree to

541 which these isotopes can retain any useful information on formation conditions, or

542 environmental interactions on anything but very short timescales.

543

544 **Acknowledgements**

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Tables

Table 1: Published results for isotope fractionation accompanying pyrolysis of C_3 and C_4 plant material.

Table 2: Summary of techniques used in radiocarbon dating of PC

Table 3: %N and δ^{15}N in wood charcoal produced from two species in laboratory charring experiments at 300-600°C, and of selected samples following exposure to 1M NaOH for 60 minutes.

Figures

Figure 1: The 'combustion continuum' and variations in the characteristics of pyrolized material along the continuum of relevance to isotope studies of pyrogenic carbon (modified from Masiello, 2004, Bird, 2006 and Conedera et al., 2009). Alteration potential refers to the degree to which the material is likely to be susceptible to chemical degradation. Transport potential refers to the degree to which the material is likely to be physicall dispersed in the environment as a result largely of particle size.

Figure 2: Carbon isotope composition of bagasse (C_4 sugarcane residue) biochar produced at three pyrolysis temperatures and then (i) buried beneath litter, or (ii) buried beneath litter and limestone chips on the surface of a tropical rainforest soil. In the case of the 300˚C biochar exposure to litter in alkaline conditions has resulted in significant ingress of C_3 rainforest-derived carbon (unpublished data).

Figure 3: Radiocarbon activity (percent modern carbon; pMC ± 2σ) of a near-radiocarbon-free biochar made in the laboratory at 450˚C ('raw') then (i) buried under leaf litter ('+litter'), or (ii) buried under leaf litter and limestone chips ('litter+lmst'), on the surface of a tropical rainforest soil for four months. After this time the samples were retrieved, with one aliquot then analysed without further treatment and the other

1162 subjected to conventional acid-base-acid pretreatment. Exposure to litter under alkaline

1163 conditions resulted in significant contamination, that was not removed by ABA

1164 pretreatment (unpublished data).

1165

1166 **Table 1:** Published results for isotope fractionation accompanying pyrolysis of C_3 and C_4

1167 plant material.

Material analysed	Regime (temperature, time, atmosphere)	$\delta^{13}C$ fractionation (‰) wrt starting material ($\Delta^{13}C_{Char}$)	Study
Grass (C3 & C4) Ash and smoke	Laboratory charring 300-700°C 0-100 min Restricted O_2.	C4 smoke: -0.5 to -7.2‰ C4 ash: <+1.0 to -3.5‰ C3 smoke: ~0‰ C3 ash: ~0‰	Das et al. (2010)
Wood (C3) Charcoal	Laboratory charring 300-600°C 60-120 mins, N_2 and 2% O_2	C3 charcoal: +0.4 to -1.6‰	Ascough et al. (2008)
Leaves (C3) Charcoal and aerosols Grass (C4) Charcoal	Natural & anthropogenic biomass pyrolysis events	C3 charcoal: -2.0‰ C4 charcoal: -9.0‰ C3 aerosol: -11.0‰	Cachier et al. (1985)
Leaves (C3) Charcoal Grass, sugarcane (C4) Charcoal Bulk aerosol, ash, CO_2 (C3 & C4)	Lab charring Flaming (>600°C) and smouldering (<200°C). CO_2 - under vacuum 150-650°C 60 min hr 850°C 120 min 850°C	C3 Aerosol : +0.5‰ C3 CO_2: ~0‰ C4 Aerosol : +3.5‰	Turekian et al. (1998)
(C3) Charcoal	Laboratory charring 30-700°C 60-120 mins; N_2	C3 charcoal: −0.5 to +2.0‰	Poole et al. (2002)
Wood (C3) Charcoal Grass (C3 & C4) Charcoal	1.) Controlled field burning 2.) Natural field burning 3.) Lab combustion 250-860 °C 20-60 min variable O_2	Field burning: C3 charcoal: ~0‰ C4 charcoal: -8.0‰ Laboratory combustion: C3 charcoal: ~0‰ C4 charcoal: ~0‰	Krull et al. (2003)
Wood (C3) Charcoal and OC volatiles	Lab charring 150-480°C	C3 charcoal: +0.3 to -1.1‰ C3 Volatiles: Variable trend	Czimczik et al. (2002)
Wood (C3) Charcoal	Lab charring 200-800 °C 30-240 min Restricted and unrestricted O_2	C3 charcoal: 0.0 to -2.0‰	Turney et al. (2006)
Wood (C3) Charcoal	Lab charring. 300-600 °C 900 min	C3 charcoal: +0.2 to -0.8‰	Jones et al. (1993)

	Ar atmosphere.		
Leaves and wood (C3 and C4) Charcoal	Lab charring. 500°C 120 min Under vacuum	C3 and C4 charcoal: 0.0 to -1.6‰	Bird and Gröcke, (1997)
Wood (C3) Charcoal	Lab charring. 300-500 °C. Restricted O_2	C3 charcoal: -0.2 to -1.9‰	Ferrio et al. (2006)
Wood (C3) Charcoal	Laboratory charring. 180-600°C Restricted O_2	C3 charcoal: +0.2 to -0.8‰	Jones and Chaloner, (1991)
Wood (C3) Charcoal	1.) Fireplace 2.) Under vacuum	C3 charcoal: Fireplace: -0.3‰ Under vacuum: -2.4‰	Leavitt, et al. (1982)

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1173   Table 2: Summary of techniques used in radiocarbon dating of PC

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treatment	comments	example references
ABA	sequential washes with acid, base and acid; simple and most commonly employed but does not guarantee contaminant removal	Hedges et al. (1989); Alon et al. (2002); Rebollo et al. (2008)
ABOX-SC	acid, base, dichromate oxidation followed by stepped combustion; complex and aggressive procedure but provides complete contaminant removal	Bird et al. (1999); Turney et al. (2001); Higham et al. (2009a)
hypy	high pressure/temperature, catalysed, reductive removal of non-polycylic aromatic organics; cheap, rapid and specific but requires specialist instrumentation	Ascough et al. (2008b)
plasma ashing	oxidation by oxygen plasma; cheap, controllable and rapid, but not specific; requires specialist instrumentation; useful where sample size is limiting	Bird et al. (2009)
compound specific	extraction and purification of molecular markers (BCPS's; PAH's); very specific but time consuming and requires specialist instrumentation	Sheesley et al. (2009); Kanke et al. (2004)

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1180 **Table 2:** %N and δ^{15}N in wood charcoal produced from two species in laboratory

1181 charring experiments at 300-600°C, and of selected samples following exposure to 1M

1182 NaOH for 60 minutes.

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		Charcoal		NaOH treated		
Species	Temperature (°C)	%N	δ^{15}N	%N	δ^{15}N	Δ^{15}N
Pinus sylvestris	Unheated	0.11	-4.4	-	-	-
	300	0.11	-4.33	0.14	-5.96	-1.63
	400	0.14	-8.05	-	-	-
	500	0.15	-7.01	-	-	-
	600	0.10	-6.06	0.11	-4.27	1.79
Rizophora apiculata	Unheated	0.16	-2.9	-	-	-
	300	0.21	-5.94	0.17	-1.57	4.37
	400	0.17	-2.07	-	-	-
	500	0.11	-2.02	-	-	-
	600	0.13	-2.92	0.22	-1.30	1.62

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