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Ascough, P.L. et al. (2009) *Hydropyrolysis as a new tool for radiocarbon pre-treatment and the quantification of black carbon*. Quaternary Geochronology, 4 (2). pp. 140-147. ISSN 1871-1014

<http://eprints.gla.ac.uk/4993/>

Deposited on: 18 October 2010

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

37

38 **Keywords**

39 black carbon, hydrolysis, radiocarbon, charcoal, biochar

40

41 **1. Introduction**

42

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

60

61 The removal of extraneous carbonaceous contaminants is essential prior to ^{14}C measurement,
62 and standard pre-treatment for pyrogenic carbon material involves sequential extraction with
63 acid and base reagents (ABA method), to remove soil carbonates and organic acids. While
64 contaminant removal is non-selective (Santos *et al.*, 2001), exact pre-treatment conditions
65 vary between laboratories, and it is not routine to empirically assess the amount or chemical
66 composition of the contaminants removed. The ABA treatment appears rapid and effective
67 for the majority of samples. However, elimination of contamination becomes more critical as
68 sample age increases, and confidence in the measured ^{14}C activity of material closer to the

69 limit of the ^{14}C method relies on the ability of a pre-treatment to exhaustively remove any
70 extraneous carbonaceous contamination. In some environments the ABA pre-treatment
71 appears not to successfully remove all contaminants (Gillespie *et al.*, 1992). For example,
72 analysis of charcoal associated with deposits from a tropical volcano indicated only partial
73 removal of residue from the decomposition of modern plant rootlets using the ABA technique
74 (Harkness *et al.*, 1994). In addition, pyrolysed biomass such as charcoal has a high affinity
75 for, and will readily adsorb, compounds such as phenols and polycyclic aromatic
76 hydrocarbons (Cornelissen and Gustafsson, 2004; Sander and Pignatello, 2005; Wang *et al.*,
77 2001). The magnitude of organic chemical sorption by BC-containing materials is variable,
78 and may be considerably larger than that exhibited by other soil organic matter (Cornelissen
79 *et al.*, 2005). Soil microbial communities also interact with pyrolysed biomass in soils (e.g.
80 Warnock *et al.*, 2007), with enhanced soil biota activity having been reported as a result of
81 factors such as relatively high availabilities of carbon and nutrients sorbed onto the charcoal
82 surface (Pietikäinen *et al.*, 2000), or through the provision of micro-habitats within the char
83 structure itself (Wardle *et al.*, 1998). In such cases, exhaustive removal of all contaminants is
84 time-consuming, and it may be difficult to remove components sorbed or weakly bonded to
85 the sample matrix without completely destroying the sample.

86

87 As BC represents carbon fixed by pyrolysis of biomass at the time of an event of interest for
88 dating, the ability to isolate and measure this component is of considerable significance for
89 ^{14}C geochronology. This is applicable both for age measurement in terms of
90 palaeoenvironmental events and also for tracer studies of environmental processes. An
91 alternative pre-treatment for samples older than 30-35 ka BP, or where conventional ABA
92 methods do not satisfactorily remove contaminants, is to remove all material apart from the
93 most chemically resistant fraction. One such method replaces the final acid wash of the ABA
94 treatment with wet oxidation, followed by stepped combustion (ABOX-SC). This technique
95 allows analysis of the most chemically resistant fraction of carbonaceous samples (Bird *et al.*,
96 1999), and has been used in age measurement of samples up to ~55 ka BP (Santos *et al.*,
97 2001; Turney *et al.*, 2001). Issues with this method include the potential release of volatile
98 sulphur compounds during evolution of sample CO_2 , resulting from the use of H_2SO_4 in the
99 oxidation step, inhibiting graphitization of the sample (Santos *et al.*, 2001). The main issue
100 with the ABOX-SC method however, is the difficulty of identifying the point at which
101 contaminants are removed and further oxidation results in degradation of the BC structure
102 itself. The amount of material isolated as BC via chemical oxidation varies depending upon

103 the source material and applied oxidation time (Knicker *et al.*, 2007). For example,
104 procedural variations in oxidation by acidified dichromate for BC isolation within a
105 systematic international inter-comparison study resulted in BC determinations from 1.1-8.0 g
106 kg⁻¹ and 0.6-2.2 g kg⁻¹ in two soils, along with variations in internal reproducibility of a factor
107 of at least 2 (Hammes *et al.*, 2007). The effective use of BC for ¹⁴C measurement therefore
108 depends upon the ability to reliably isolate and analyse this material from a range of
109 environmental matrices. Attempts to improve current analytical techniques are complicated
110 by the fact that methodological developments for BC isolation are ongoing, and that various
111 existing methodologies define BC according to different criteria, depending upon the part of
112 the pyrogenic carbon continuum they target (Preston and Schmidt, 2006). Some methods may
113 also result in methodological artefacts. For example, Simpson and Hatcher (2004) found that
114 a thermal oxidative method for BC quantification inadvertently produced a component of
115 pyrolysed organic matter subsequently defined as BC during analysis of initially BC-free
116 material. Research aims have therefore included the development of methodologies that
117 reduce the potential for artefacts and allow greater accuracy in BC quantification (e.g.
118 Gelinis *et al.*, 2001).

119
120 Significant research benefits are therefore offered by a technique that can effectively and
121 reproducibly isolate and quantify purified BC from a wide range of sample matrices. In this
122 paper, we explore the potential of a new method which holds great promise in this regard,
123 known as hydroxylation (hypy). Hypy uses pyrolysis assisted by high hydrogen pressures
124 (>10 MPa) with a dispersed sulphided molybdenum (Mo) catalyst to separate labile and
125 refractory carbonaceous sample components. This process has been used extensively in
126 analysis of terrestrial kerogens where overall conversions of close to 100% are achieved for
127 thermally labile material (e.g. Roberts *et al.*, 1995), the principal product being a
128 dichloromethane-soluble oil. Further, it has been shown that the hydrocarbon products of
129 hypy are released in high yields (Love *et al.*, 1997), with the advantage that it should be
130 possible to identify and characterize the non-BC contaminants in samples at a molecular
131 level, as well as being able to measure the ¹⁴C activity of the compounds removed by hypy.
132 Because stereochemical rearrangements accompanying hypy are minimal due to the high
133 pressure hydrogen, the neoformation of BC that occurs in normal thermal oxidation is
134 suppressed, meaning that interference from formation of BC during the analytical procedure
135 should not occur (Love *et al.*, 1995).

136

137

138 In general, hypy offers a potential means to discriminate between bound and adsorbed
139 organic species. As a result, the technique has been used to remove adsorbed products,
140 facilitating analysis of organic carbon in samples even up to Archaean age (Brocks *et al.*,
141 2003). Thus far, however, the potential application of hypy for the quantification and
142 isolation of BC for ^{14}C measurement remains unexplored. In this study, we have used a range
143 of samples containing BC of various antiquities and in various soil matrices to assess the
144 utility of hypy as an efficient tool for radiocarbon pre-treatment and BC quantification. One
145 key factor is whether it is possible to determine the operational conditions under which
146 removal of the labile organic matter is complete. At this point, further hydrogen pyrolysis
147 would result in degradation of the purified BC itself via hydrogasification. We have therefore
148 assessed the reproducibility and reliability of the method to isolate BC from soils and
149 charcoal, and used ^{14}C measurement of the hypy residue and removed products to test its
150 potential utility as a pre-treatment procedure for ^{14}C analysis of charcoal.

151

151 **2. Materials and methods**

152

153 **2.1. Samples**

154

155 Information on the samples selected for this study is provided in Table 1. These include three
156 ancient charcoals obtained from natural and archaeological deposits, two of which are from
157 deposits of key geological and archaeological significance, close to the radiocarbon dating
158 boundary, with previously established ^{14}C ages. The first of these charcoal samples (MA) was
159 recovered *in situ* from paroxysmal flow deposits source from the Maninjau caldera in west-
160 central Sumatra. Isothermal plateau and diameter corrected fission-track techniques place the
161 flow deposits at $50,000 \pm 3000$ BP (Alloway *et al.*, 2004). For MA, the previous ^{14}C
162 measurements included pre-treatment by conventional ABA and ABOX-SC pre-treatment,
163 giving ages of $51,100 \pm 3200$ to $52,300 \pm 2000$ ^{14}C BP, and earlier assessments of infinite
164 ages $>40,000$ ^{14}C BP (Table 1).

165

166 The second charcoal sample, CHA, was recovered from a hearth deposit in the Megaceros
167 gallery of Chauvet Cave, in the Ardeche Valley of France. Human activity in the cave
168 included the oldest parietal art thus recorded, dated to ca. 32,000 years BP (Clottes *et al.*,
169 1995, Valladas *et al.*, 2001 and Valladas *et al.*, 2005), and along with charcoal, associated
170 deposits containing animal skeletal remains, animal and human footprints, and flint and ivory
171 artefacts (Garcia, 2005 and Geneste, 2005). The charcoal sample obtained from material
172 excavated at Chauvet Cave (CHA) had previously been subjected to ^{14}C measurement as part
173 of a laboratory intercomparison exercise (Cuzange *et al.*, 2007), as part of which the ABOX-
174 SC pre-treatment methodology was used for some measurements, yielding ages of $32,350 \pm$
175 210 to $31,810 \pm 190$ ^{14}C BP (Table 1). The results of multiple ^{14}C measurements on charcoal
176 samples from the hearth from which CHA was sampled yielded an average age of $32,030 \pm$
177 120 ^{14}C BP (Cuzange *et al.*, 2007).

178

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

184

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

195

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

206

207 **2.2. Hypy procedure**

208

209 Fixed bed hypy tests were performed using the apparatus shown in Figure 1, with the
210 products collected in a silica filled trap (Meredith *et al.*, 2004) immersed in a dry ice slush
211 trap. The procedure is described in detail in Love *et al.*, (1995; 1997). Briefly, the samples
212 were first loaded with the Mo catalyst (5% by weight) using an aqueous/methanol 0.2M
213 solution of ammonium dioxodithiomolybdate $[(\text{NH}_4)_2\text{MoO}_2\text{S}_2]$, and then pyrolysed with
214 resistive heating from 50C to 250C at 300C min^{-1} , and then from 250C to the final
215 temperature (between 400 and 600C) at 8C min^{-1} , under a hydrogen pressure of 15 MPa. A
216 hydrogen sweep gas flow of 5 L min^{-1} , measured at ambient temperature and pressure,

217 ensured that the products were quickly removed from the reactor vessel. Three replicate tests
218 to a final hold temperature of 500°C were performed on the MO soil sample to assess
219 reproducibility of the hypy technique.

220

221 **2.3. Determination of non-BC removal using hypy**

222

223 Tests were performed in order to ascertain whether it was possible to observe a plateau with
224 increasing temperature corresponding to a temperature interval after the removal of labile
225 organic matter is complete (i.e. non-BC material, mainly lignocellulosic) and before the onset
226 of hydrogasification of the BC itself to methane (e.g. Suzuki *et al.*, 1986; Bolton *et al.*, 1987;
227 Xua *et al.*, 2003). This involved monitoring the residual Total Organic Carbon (TOC) content
228 of VER and BGS reference soils and charcoal sample MA as a function of the peak
229 temperature used in each hypy test. Hypy temperature was varied between 400 and 600°C at
230 increments of 25°C for the soils and between 500 and 600°C for the charcoal. For MA, the
231 total mass loss of the sample was determined for each experiment. The TOC of samples were
232 measured using a CO₂ coulometer (UIC[®] Coulometrics Inc., IL, USA), which measures the
233 CO₂ generated by combustion of the sample at 1000°C in a stream of oxygen by titration
234 against ethanolamine. For each sample the average of two replicate analyses was taken.

235

236 **2.4. Hypy procedure for ¹⁴C measurement**

237

238 After the hypy treatment the sample residue and the hypy product, cryogenically collected on
239 silica (i.e. removed contamination), were AMS dated at the ORAU (Oxford Radiocarbon
240 Accelerator Unit), University of Oxford. ¹⁴C measurements were also made of aliquots of the
241 untreated charcoal and charcoal treated with 0.5M HCl for decarbonation (as described
242 below). For δ¹³C measurements, samples were combusted and analyzed using a Europa
243 Scientific IRMS system interfaced to a Roboprep CHN sample converter unit, operating in
244 continuous flow mode using helium as the carrier gas. Stable isotope ratios are expressed in
245 ‰ relative to vPDB where mass spectrometric precision is ± 0.2‰. The ¹⁴C content of
246 charcoal reflects that of atmospheric sources at the time the plant grew, and thus reflects a
247 relatively constrained time interval. In this instance, the event of interest for dating, (i.e. the
248 date of plant tissue formation), corresponds to a single, constrained and hence 'dateable'
249 event. This contrasts with the BC component of the soil samples, as it is likely that this

250 represents a mix of inputs from different sources over an extended but unknown period.
251 Therefore, while the soil samples represent well-characterized standard materials, they are
252 otherwise uncontextualized, limiting our ability to interpret a ^{14}C measurement of these
253 samples following hypy in a meaningful manner. Hence we did not measure the ^{14}C activity
254 of the soil samples.

255

256 The charcoal samples for ^{14}C determination were crushed to pass a 500 μm mesh, and an
257 aliquot of the crushed material (i.e. with only physical treatment) was taken for dating as
258 representative of the untreated sample. The remaining sample material was then placed in
259 0.5M HCl overnight to remove soil carbonates. Following decarbonation the sample was
260 washed three times in deionized water before drying to constant weight at 50°C. An aliquot of
261 the decarbonated charcoal was subjected to standard ABA pre-treatment at the University of
262 Oxford (c.f. Wild et al., 2008). This consists of an acid wash to remove sediment carbonates,
263 a base wash to remove organic acid contaminants such as humic acids and a final acid wash
264 (to remove any atmospheric CO_2 which may have been absorbed by the sample during the
265 base wash). In between each wash the samples were thoroughly rinsed with ultrapure water.

266

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

277

278

279

279 3. Results

280

281 3.1 BC determination via hypy

282

283 The change in residual TOC as a function of temperature for the VER and BGS reference
284 soils and the MA charcoal is presented in Table 2 and Figures 2 and 3. Mass losses during
285 hypy of the soil samples were c. 2-3% w/w. Figure 2 shows the same trend of decreasing
286 carbon content until 550°C for VER and 525°C for BGS, corresponding to the loss of carbon
287 from the labile (i.e. non-BC) organic matter in the soil. Following this phase a plateau in
288 TOC is reached. This is consistent with other hypy studies for lignocellulosic material which
289 has indicated that up to 100% conversion to volatile products is achieved by approximately
290 500°C (Rocha et al., 1999). At 600°C, following the plateau phase, there is the beginning of a
291 further loss of carbon which marks the onset of BC hydrogasification to yield methane. The
292 residual TOC content over the plateau region is taken as the BC content of the sample
293 material, and represents the conditions under which the total BC portion of a sample may be
294 recovered. For VER at 550°C this suggests a BC content of 6.6 g kg⁻¹ which is consistent
295 with, but at the upper end of, values obtained for this sample in the BC inter-comparison
296 study (e.g. 4.7±2.9 g kg⁻¹ for dichromate oxidation (Hammes *et al.*, 2007)). For the BGS
297 sample at 550°C the estimated BC content is 28.5 g kg⁻¹, which is comparable with previous
298 BC determination for this sample of 24.3 g kg⁻¹. These results provide strong evidence that at
299 temperatures above c.500⁰C non-BC sample components are effectively removed.

300

301 Clearly, depending where a particular sample lies within a broad continuum of compositions,
302 some weight loss might be anticipated during hypy, especially those samples that have not
303 been subjected to high temperature during initial pyrolysis. This is supported by the tests on
304 the MA charcoal sample, where sample weight loss during hypy increases from 14.1% by
305 500°C to 26.8% by 600°C where it then appears to level off (Figure 3). Much of the weight
306 loss below 500°C is due to oxygen removal which gives rise to the increase in the TOC
307 content relative to the initial (catalysed) sample (Table 2) but some carbon loss from the
308 sample itself has also occurred. Most of the mass loss of the MA sample between 500 and
309 575°C is also due to oxygen as indicated by the fairly constant level of TOC remaining over
310 this temperature range. However, a small quantity of tar was collected, which may be
311 derived from the decomposition of highly aromatic humic acids (Haumaier and Zech, 1995).

312 The apparent plateau in the MA sample still evident at 600°C could represent a delayed onset
313 of hydrogasification in relation to the two soil samples. The uncertainty in the BC
314 determination arising from this extended plateau however is clearly very small compared to
315 the high variations described earlier for oxidative procedures.

316

317 **3.2 Reproducibility**

318

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

325

326 **3.3. ^{14}C analysis**

327

328 The results of the ^{14}C measurements are listed in Table 3. Results for the MA charcoal
329 residue extracted by hypy ($51,200 \pm 1100$ ^{14}C BP; Figure 4(A)) are consistent with previous
330 measurements of this sample (Table 1). ^{14}C measurement of the untreated sample is also
331 consistent with these analyses, demonstrating that for this sample, the level of environmental
332 contamination does not significantly affect its ^{14}C age. Results for the aliquot of MA (OxA-
333 16319; $46,600 \pm 700$ ^{14}C BP) that had been subject to 0.5M HCl digestion and deionized H₂O
334 washing prior to ABA pre-treatment and ^{14}C measurement do however suggest either that one
335 or more of these treatments can introduce trace amounts of contamination. Analysis of the
336 product of hypy (retained on silica following removal from the pyrogenic carbon sample)
337 gives a ^{14}C age of $37,450 \pm 750$ ^{14}C BP. This indicates that carbon contamination younger
338 than the ^{14}C age of the initial sample, albeit present in small amounts, is removed in the hypy
339 treatment.

340

341 ^{14}C measurement of the untreated sample of CHA (Figure 4(B)) shows that, in common with
342 MA, environmental contamination by younger carbon does not significantly affect the bulk
343 sample $^{14}\text{C}/^{12}\text{C}$ ratio, as this measurement, $32,370 \pm 180$ ^{14}C BP (OxA-V-2211-17), is
344 consistent with previous determinations performed within the laboratory intercomparison
345 exercise (Cuzange *et al.*, 2007). This conclusion was also drawn by Cuzange *et al.*, (2007),

346 following ^{14}C measurement of the alkali-soluble fraction of Chauvet Cave charcoals, which
347 were not found to be significantly different from the purified charcoal following conventional
348 pre-treatment. Measurement of the aliquot of CHA subject to 0.5M HCl treatment gives an
349 age of $31,990 \pm 180$ ^{14}C BP (OxA-17090) following ABA pre-treatment and $31,150 \pm 250$
350 ^{14}C BP (OxA-V-2211-16) following hypy treatment. The products of hypy extraction of the
351 CHA sample on silica were dated to $28,050 \pm 310$ ^{14}C BP (OxA-V-2198-50), again
352 significantly younger than that of the hypy residue, indicating selective removal of
353 contamination present in small amounts. It is important also to note that, as well as younger
354 contamination, samples may also be affected by older exogenous carbon, with a lower ^{14}C
355 activity to that of the sample. In the case of CHA, the untreated ages appear slightly older
356 than those subject to pre-treatment, which may indicate the presence of older, possibly
357 geological, material.

358

359 Analysis of the high ^{14}C activity Holocene charcoal sample (CAS), presented in Figure 4(C),
360 showed that again, environmental contamination present in the sample does not appear to be
361 sufficient to influence the ^{14}C age, as the age of the untreated sample (2732 ± 29 ^{14}C BP) is
362 within analytical error of the treated sample ages. In this instance, aliquots of CAS subject to
363 0.5M HCl treatment give similar ages whether treated by ABA (2723 ± 28 ^{14}C BP) or hypy
364 (2748 ± 28 ^{14}C BP). In addition, the age of the material extracted by hypy onto silica ($2732 \pm$
365 28 ^{14}C BP) is also similar to that of the purified charcoals. This indicates that the non-BC
366 material in this sample is either not of a significantly different ^{14}C activity to that of the BC
367 material fixed by pyrolysis during sample formation, or is present in trace quantities
368 insufficient to influence the measured age of this more recent age sample.

369

370

370 4. Discussion

371

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

385

386 In the case of MA, the introduction of carbonaceous material with a different ^{14}C age to that
387 of the resistant BC sample fraction appears to influence the sample ^{14}C age following
388 standard ABA pre-treatment, although this is not apparent in the case of CHA. Hatté *et al.*
389 (2001) suggested that during the NaOH step of the ABA pre-treatment atmospheric CO_2
390 dissolved into the solution might become linked with electropositive ions or incorporated
391 directly with functional groups within the sample. They found that final acidification with
392 HCl was not sufficient to remove this and break these ionic links, but that H_2SO_4 or ABOX-
393 SC treatments were. The samples tested in this earlier study did not include pyrogenic carbon,
394 and it is possible that similar trace contamination is responsible for the younger observed ^{14}C
395 age of MA following ABA treatment. In both instances the hypy treatment appeared to
396 remove contaminating carbon from the samples, yielding ages that are in accord with
397 previous age measurements at several laboratories.

398

399 The ^{14}C age of the material removed by the hypy process from MA and CHA, although
400 higher than that of the residue, is still relatively ancient ($37,450 \pm 750$ ^{14}C BP and $28,050 \pm$
401 310 ^{14}C BP respectively). This indicates that the hypy process is removing parts of the sample
402 matrix itself that are susceptible to contamination, leaving the inert portion unaffected.
403 Following formation by pyrolysis, charcoal may comprise a range of carbon species which

404 are not all in condensed aromatic form and therefore may provide sites for the adsorption of
405 contaminating carbon. If the ABA pre-treatment does not always fully remove these sample
406 components, this may explain the younger age of the ABA treated MA charcoal, whereas
407 hypy does seem to selectively target contaminants. One advantage of the method in this
408 context is that material removed in the hypy process may itself be subject to further analysis
409 as it is retained by cryogenic trapping. These results indicate the potential of hypy as a pre-
410 treatment technique for ^{14}C age measurement of samples with a constrained, continuous
411 formation period. This could be extended to the separation of specific carbon fractions in
412 more complex samples, such as soil, in order to calculate aspects such as cycling and
413 turnover of the resistant carbon fraction. Effective application of hypy for these purposes
414 however requires more extensive investigation to establish the technique in matrices
415 containing more thermally labile organic carbon and carbonates.

416

417 It is important to note that, for the charcoal samples tested here, environmental contamination
418 does not appear to have introduced a significant amount of extraneous carbon with a different
419 ^{14}C age to that of the sample. Chauvet Cave is located within the deep karst development of
420 the Ardèche Plateau (Mocochain *et al.*, 2006), therefore input from geological ^{14}C -dead
421 carbonates to the sample during deposition is a possibility. The results from this study
422 however support previous conclusions that if such contamination is present, it is in small
423 amounts that do not significantly influence the overall sample ^{14}C activity (Cuzange *et al.*,
424 2007). One possibility for the apparent absence of evidence for post-depositional
425 environmental contamination in MA is a result of the emplacement of this sample in
426 pyroclastic flow of poorly sorted pumicious lapilli and ash (Alloway *et al.*, 2004) where
427 processes such as organic carbon decomposition and soil carbon cycling have not provided a
428 means for contamination. Interestingly, in the sample recovered from Holocene sediments
429 modified by the presence of a human domestic fortified settlement (Valera, 1997), ^{14}C
430 measurement of the untreated sample also indicates no evidence of environmental
431 contamination, as the untreated and treated (both ABA and hypy) samples give the same age.
432 In this instance, the ^{14}C age of the material removed during the hypy process is also
433 indistinguishable from the treated and untreated sample ages, indicating that the amounts of
434 contaminating material introduced during processing are very slight, and therefore
435 insufficient to influence the age of much younger samples with high ^{14}C activity.

436

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

457

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

467

468

468 **5. Conclusions**

469

470 The fact that hypy can reduce labile organic matter to volatile products in a controlled
471 manner makes it an attractive new approach for the rapid isolation of the most resistant BC
472 fraction from carbonaceous samples. This suggests that hypy represents a promising new
473 approach not only for BC quantification as an end in itself, but also for ^{14}C dating where
474 purified BC is the target material for dating. These two goals are combined in many research
475 studies, for example in efforts to establish the persistence and resistance of BC in the
476 environment, and to quantify BC production rates and turnover times over extended
477 timescales. The findings obtained here for soils and charcoal, in conjunction with the
478 previously reported findings for lignocellulosic material, coals, and
479 petroleum source rocks, suggest that hydrolysis is potentially a precise method for BC
480 measurements in a range of sample materials. Further investigation of the applicability of
481 hypy for these purposes should focus upon additional characterization of the hypy solid
482 residue and products, particularly with use of spectroscopic methods, for example solid-state
483 ^{13}C nuclear magnetic resonance, which have been useful within studies of a wide range of
484 BC-containing matrices (e.g. Simpson and Hatcher, 2004).

485

486 Further investigation of hypy applicability for ^{14}C measurement would benefit via analysis of
487 BC materials previously shown to have suffered modern contamination. It appears that the
488 method is potentially particularly effective for pre-treatment of samples close to the ^{14}C
489 dating limit, where even trace contamination may be sufficient to produce a significant shift
490 in measured sample isotopic ratio. An important additional advantage of the hypy technique
491 is that it allows retention of the non-BC component of a sample, which may then be subject to
492 further analysis and measurement. In applying the method to ^{14}C pre-treatment of charcoal
493 where sample size is not limiting, it may be advantageous to select a more aggressive hypy
494 regime, leading to some removal of the most resistant BC carbon itself by hydrogasification
495 to ensure complete removal of all trace contaminants. However, it is also conceivable that the
496 method could be used for simultaneous BC quantification and sample purification for ^{14}C
497 analysis.

498

499

499 **Acknowledgements**

500 Funding for this work was provided by NERC standard grant NE/C004531/1 'Charcoal
501 Degradation in Natural Environments'. C.H. Vane publishes with permission of the
502 Executive Director, British Geological Survey. The authors acknowledge Helène Valladas,
503 Bruno David and Antonio Valera for kindly providing samples of archaeological charcoal for
504 analysis in this project, coordinating members of the Black Carbon ring trial (Hammes *et al.*,
505 2007) for samples of soil standard BC reference materials, and the staff of the Oxford
506 Radiocarbon Accelerator Unit for analyses. This work represents a contribution for the
507 Scottish Alliance for Geosciences, Environment and Society (SAGES).

508

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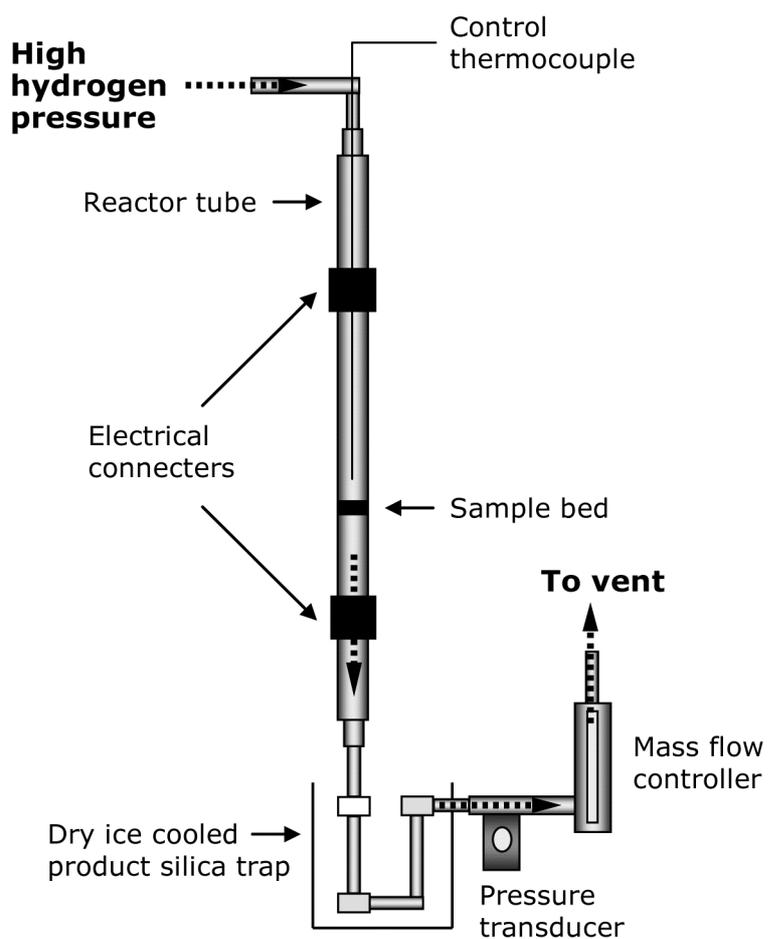
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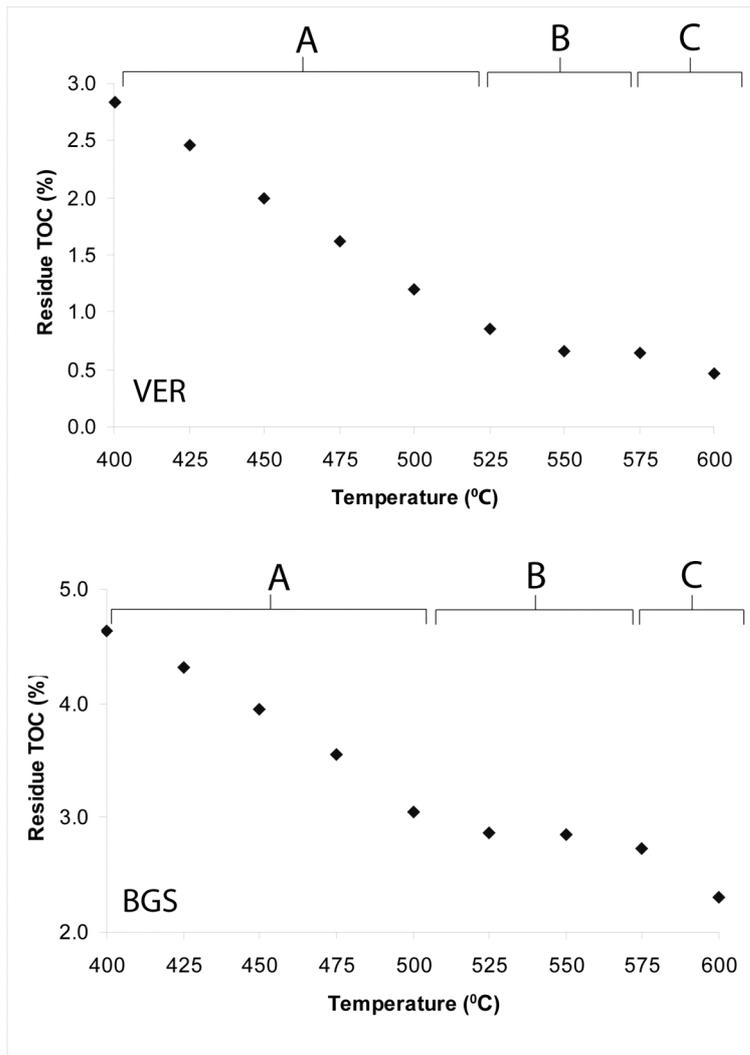
721 **Figure legends**



722

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

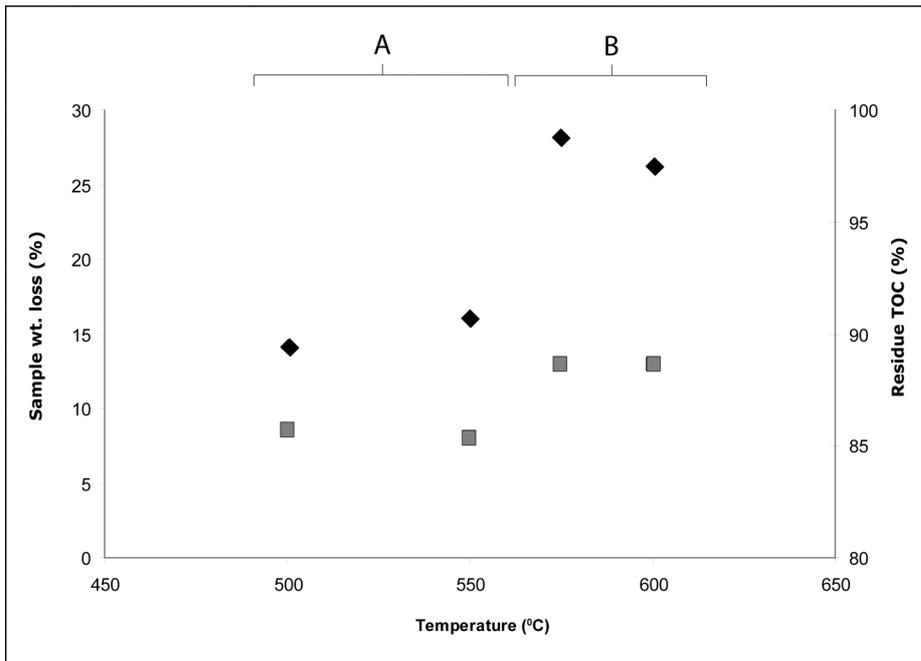
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726

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

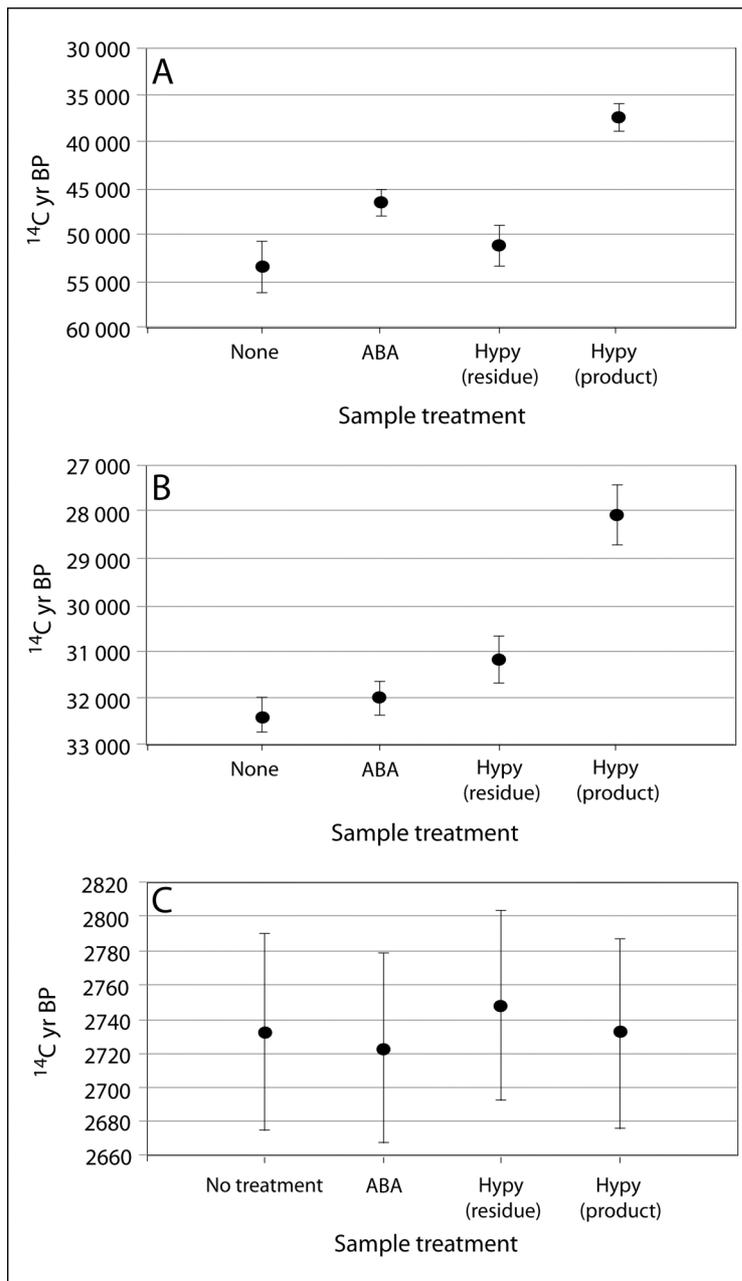
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731

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

736



737
 738 Figure 4: ^{14}C measurement results of the charcoal samples following no treatment, and pre-
 739 treatment with standard ABA and hypy methodologies. For samples treated by hypy both the
 740 products removed from the charcoal during treatment (product), and the BC residue
 741 following hypy were analysed. Samples are presented in order of age, where A: MA, B:
 742 CHA, and C: CAS.

743

744

744 **Table legends**

Sample code	Material	Deposition location	Previous age assessments (^{14}C BP) ²	Clay content (mass %) ³	TOC (g kg ⁻¹) ³	Previous BC assessments (g kg ⁻¹) ³
MA	Charcoal (species unknown)	Maninjau, Sumatra	51,100 ± 3200 (Wk-13370) 52,300 ± 2000 (ANUA -13404/-14112) >40,000 (Wk-5370) >47,000 (NZA-9396)			
CHA	Charcoal (species unknown)	Chauvet Cave, Dordogne, France	32,350 ± 210 (OxA-X-2130-47) 32,080 ± 200 (OxA-X-2131-14) 31,810 ± 190 ^{14}C BP (OxA-X-2130-48)			
CAS	Charcoal (<i>Quercus suber</i> L.)	Castro de Santiago, Portugal	Previously undated			
VER	Vertisol BC ring trial standard ¹	Queensland, Australia	Previously undated	70.0	27.3	4.7 ± 2.9
MO	Mollisol BC ring trial standard ¹	Hildesheim-Braunschweig, Germany	Previously undated	23.9	17.8	1.4 ± 0.9
BGS	Industrial soil standard	Glasgow, Scotland, UK	Previously undated	35.0-55.0	58.2	24.3

745

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

748 ¹Hammes *et al.*, 2007.

749 ²Alloway *et al.*, 2004; Cuzange *et al.*, 2007.

750 ³Skjemstad *et al.*, 1999; Schmidt *et al.*, 1999; Schmidt *et al.*, 2001; Hammes *et al.*, 2007;
751 Rawlins *et al.*, 2008.

752

753

754

Sample	Vertisol TOC (± 0.05%)	BGS TOC (±0.05%)	Maninjau TOC (± 0.5%)	Maninjau weight loss (%)
Initial	3.47	5.75	81.3	-
Catalysed	3.21	5.57	77.4	-
400C	2.82	4.63	-	-
425C	2.46	4.31	-	-
450C	2.00	3.95	-	-
475C	1.63	3.55	-	-
500C	1.19	3.06	85.7	14.1
525C	0.85	2.87	-	-
550C	0.66	2.85	85.4	16.1
575C	0.64	2.73	88.6	28.2
600C	0.47	2.31	88.6	26.2

755 () = % of original TOC remaining after hypy.

756

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

759

Sample	Laboratory code	Treatment	$\delta^{13}\text{C}$ (‰)	Age BP (^{14}C years $\pm 1\sigma$)
MA	OxA-V-2190-49	None	-23.5	53400 \pm 1400
	OxA-16319	ABA	-24.5	46600 \pm 700
	OxA-V-2190-47	Hypy residue	-23.1	51200 \pm 1100
	OxA-V-2198-48	Hypy product	-23.6	37450 \pm 750
CHA	OxA-V-2211-17	None	-22.5	32370 \pm 180
	OxA-17090	ABA	-22.7	31990 \pm 180
	OxA-V-2211-16	Hypy residue	-22.1	31150 \pm 250
	OxA-V-2198-50	Hypy product	-22.9	28050 \pm 310
CAS	OxA-V-2190-56	None	-22.8	2732 \pm 29
	OxA-16756	ABA	-23.2	2723 \pm 28
	OxA-V-2190-57	Hypy residue	-22.2	2748 \pm 28
	OxA-V-2198-49	Hypy product	-22.8	2732 \pm 28

760

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

766