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Assessment of oxygen plasma ashing as a pre-treatment for radiocarbon dating

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Abstract

This study investigates the potential of low-temperature oxygen plasma ashing as a technique for decontaminating charcoal and wood samples prior to radiocarbon dating. Plasma ashing is demonstrated to be rapid, controllable and surface-specific, and clear differences are identified in the rate of ashing in different organic materials. However, the ability of plasma ashing to selectively remove these different components is limited in heterogeneous sample matrices. This is because oxidation is confined to the immediate sample surface. Comparison of radiocarbon dates obtained from identical aliquots of contaminated ancient charcoal pre-treated by acid-base-acid (ABA), acid-base-oxidation-stepped combustion (ABOx-SC) and plasma ashing suggests that the technique performs as well as the ABA pre-treatment but does not remove as much contamination as the ABOx-SC technique. Plasma-ashing may be particularly useful in cases where sample size is limiting.

1. Introduction

Radiocarbon (^{14}C) dating of both charcoal and wood has underpinned development of the precise chronologies required to understand archaeological and environmental change over the last ~50,000 years. A prime requirement for successful dating is that the carbon in a sample is not contaminated by exogenous carbon of either older or younger age. Removal of such contaminants becomes more critical as the age of a sample increases, particularly if contamination is younger than the sample being dated (Bird, 2006).

Many pre-treatment techniques have been developed in order to remove contaminant carbon prior to ^{14}C dating. In the case of charcoal, the most commonly applied protocol involves sequential treatment with acid-base-acid (ABA). This treatment is designed to remove carbonates, humic acids and adsorbed CO_2 respectively (e.g. Alon et al., 2002). More recently, the ABOx-SC (acid-base-oxidation with stepped combustion) has been shown, in some circumstances, to provide more reliable contaminant removal from charcoal, enabling robust dating of charcoal as old as 55 ka BP (Bird et al., 1999, 2003; Turney et al., 2001; Brock and Higham, in press). In the case of wood, both ABA and ABOx-SC have been successfully used to pre-treat samples over a variety of age ranges (e.g. Santos et al., 2001; Gaudinski et al., 2005).

All the above techniques are time intensive and require multiple chemical steps that may contribute to the laboratory handling blank associated with an analysis. Both the ABA and the ABOx-SC pre-treatments have the additional major disadvantage that there is currently no way of pre-determining the degree to which a sample will be susceptible to dissolution/oxidation (Bird et al., 2002; Brock and Higham, 2009; Rebollo et al., 2008). In practice this means that some samples rapidly undergo virtually complete dissolution/oxidation, when only a small proportion of the material that is lost in pre-treatment is likely to be an exogenous contaminant. This is a serious issue as it means that potentially significant samples, on occasion, are not dateable due to excessive removal of material during pre-treatment.

Low-temperature oxygen plasma ashing is a surface active technique that uses a low pressure of oxygen gas excited by a radio frequency generator to oxidize organic material (e.g. Dai, 1996) without raising the sample temperature beyond c.150˚C, with maximum temperature decreasing as radio frequency (RF) power is decreased (Emitech, unpubl. data). In Quaternary studies, the technique has been used to remove organic carbon from carbonate and sediment samples, and also to liberate and collect CO_2 for radiocarbon dating from a range of archaeological materials (Russ et al., 1990; Rowe and Steelman, 2003; Steelman et al., 2004).

Given that plasma ashing is surface-active, rapid, involves only oxygen as a reagent, and the rate of ashing can be readily controlled by changing the RF power applied to the oxygen plasma, it would appear to hold promise as a widely applicable technique for the pre-treatment of a range of organic samples to remove contamination prior to radiocarbon dating. It is the purpose of this study to assess the utility of plasma ashing in this regard. In the first part of the study we use modern and ancient charcoals as well other materials to elucidate the controls on sample behaviour during ashing. In the second part of the study we apply plasma ashing to a number of archaeological charcoals known to be contaminated by ‘young’ carbon in order to assess the effectiveness of the technique for routine sample decontamination.

2. Materials and methods

2.1 Plasma ashing tests

The samples used to test the plasma ashing methodology represent (i) wood, (ii) charcoal produced in the laboratory under known pyrolysis conditions, (iii) charcoal from sedimentary deposits, (iv) highly-ordered pyrolytic graphite (HOPG) (v) microcrystalline cellulose and (vi) sucrose (Table 1). The HOPG was included in the study to determine the effect of plasma ashing on highly crystalline graphitic carbon. The other non-charcoal samples were included to determine the effects of ashing on a range of organic carbonaceous material of relevance to radiocarbon dating.

The modern wood was birch (*Betula pubescens* Braw) obtained from Iceland. Laboratory charcoal was produced at 300˚C and 600˚C (B300 and B600) from aliquots of the modern wood. This was achieved using a Carbolite controlled atmosphere rotary furnace, set at a heating rate of 10˚C min^{-1} to the nominated pyrolysis temperature and held at that temperature for 120 mins while being continuously purged with nitrogen at a constant metered flow rate of 7 L/min.

Charcoal samples from sedimentary deposits were analysed to determine whether environmental exposure alters plasma ashing behaviour. These samples include charcoal produced from birch wood in Iceland (REU and HOSK) in Norse charcoal production pits during the first millennium AD (Church et al., 2007). A further two natural charcoal samples, AZ and 73614, were obtained from lahar deposits (AZ), in the northwest of Faial Island, Azores (F. Tempera, pers comm.), and at Toca do Serrote da Bastiana (73614), a rock shelter in northeast Brazil (Guidon, N., pers comm). These were included in this study as they were found, through initial NMR analysis to be composed of a range of compounds in addition to the polyphenolic compounds characteristic of pyrolysed biomass (e.g. Ascough et al., 2008).

All samples were crushed, treated with 0.5 M HCl overnight at room temperature to remove carbonates, washed and dried. They were then sieved and the 63-500 μm fraction retained for further analysis. Aliquots of 63-500 μm material were further crushed to pass a 63 μm sieve in some cases, to assess the effect of particle size on ashing rate and effectiveness of decontamination. Ashing was undertaken using an Emitech K1050X plasma asher operated at between 2 and 100 W of forward power, at a vacuum of 0.2 mbar with an oxygen flow rate of 10 ml/min.

For each analysis an aliquot of 40 ± 5 mg was accurately weighed into an aluminium weighing boat and then ashed initially at time steps of 15 min, increasing progressively to time steps of up to 5 h. Between successive ashing steps, the weighing boat plus remaining sample was reweighed to develop an oxidation curve. Initial experiments confirmed that the weight of the aluminium weighing boat was not affected by the ashing process, and replicate runs suggest that the results are in all cases reproducible to better than ±1% of the sample mass with an average reproducibility of ±0.6% (n=30). All results are corrected for ash content using the loss on ignition results in Table 1 and are reported on an equivalent ash-free basis.

The stable carbon isotope compositions ($\delta^{13}C$ value) of selected samples were determined using a Costech elemental analyser coupled to a Thermo-Finnigan Delta Plus XL mass spectrometer operated in continuous flow mode. Results are reported relative to the V-PDB scales with an uncertainty of ±0.1‰ determined from the analysis of internal standards.

^{13}C-CP-SSNMR spectra were recorded on a 500 MHz Varian Infinityplus or a Varian VNMRS spectrometer, operating at a ^{13}C frequency of 75.398 and 100.56 MHz respectively, at ambient temperature. The 300 MHz spectra were recorded using a 5 mm Chemagnetics Apex probe and the VNMRS spectra using a 4 mm MAS probe. Spinning speeds were between 7 and 12 kHz with a CP contact time of 1 ms and a 1 s recycle time, and spectral referencing was with respect to tetramethylsilane. A rotor-synchronized spin-echo was used to suppress a broad probe background signal.

2.2 radiocarbon dating

In order to test the capacity of plasma-ashing to effectively decontaminate samples for radiocarbon dating, three samples known to contain a component of contamination not removed by the conventional ABA treatment (Brock and Higham, 2009), were ashed at 18 W and submitted for radiocarbon dating (Table 3). Two samples were from hearths in the Proto-Aurignacian level A2 of Grotta di Fumane, Italy. In Italy, the Proto-Aurignacian is always found beneath the Campanian Ignimbrite tephra, dated by $^{40}Ar/^{39}Ar$ to 39,280±110 cal BP (de Vivo et al, 2001). Therefore, although the tephra has not yet been found in Fumane, the

Proto-Aurignacian is highly likely to predate c.39,000 cal BP (Brock and Higham, 2009). A further sample is from level XIX from the Mousterian site of Esquilleu, Spain. This level is compact and brecciated, limiting the potential for movement of the charcoal fragment from higher contexts. Previous ABA radiocarbon dates on charcoal place the later levels XVIII and XIII at 49700±1600 BP (OxA-11414) and 39000±300 BP (Beta-149320) respectively (Baena et al., 2005; Baena et al,, 2006).

The samples were treated with concentrated sulphurous acid to remove carbonates, dried, and prior to ashing, were crushed to fine powder (<63 μm) in order to expose the maximum surface area to the oxygen plasma. Sulphurous acid was chosen because it leaves no residue on drying. 15-50 mg of each of the charcoals were then ashed to 50-80% of their starting mass. In order to further examine the effect of progressively longer ashing, the Esquilleu sample was ashed until 42% mass was lost, before being re-crushed and ashed until 60% had been lost. This was done in order to determine whether more efficient deconamination could be achieved by exposing new surfaces to the plasma.

All samples were washed in 1 M HCl at 80˚C for 20 min and rinsed three times in ultrapure water (MilliQ™) to ensure the removal of remaining sulphur from the initial acid wash as well as any contaminants absorbed between the plasma oxidation and arrival in the radiocarbon laboratory. Where ABOX-SC pre-treatment was performed, this followed the procedures of Brock and Higham (2009). Graphite targets were prepared and measured in the Oxford Radiocarbon Accelerator Unit (ORAU) as described by Brock and Higham (2009).

As is standard practice within ORAU, modern (Owen Buddleia) and ancient (Maninjau) charcoal standards were treated with ABA, ABOx-SC and plasma oxidized samples to monitor laboratory contamination.

3. Results

3.1 Plasma ashing experiments

Initial experiments to determine the effect of ashing on a highly crystalline graphitic material (HOPG) suggest that crystalline graphite oxidizes only very slowly at RF powers of 10 W and below. However the rate of oxidation increased dramatically as power is increased to a maximum of 100 W, with <63 μm HOPG ashing significantly faster than 63-500 μm HOPG at all powers above 2 W (Figure 1A). Ashing of HOPG over 600 mins at 5 W suggests minimal rates of loss of 0.5%/h for the <63μm fraction and 0.04%/h for the 63-500μm fraction.

The responses of all other samples to ashing ranged from quasi-linear to quasi-exponential, with rate of oxidation increasing as RF power increased (Figure 1B-H). Wood and charcoal samples ashed to 50% of their original mass over 10 to 1000 mins depending on sample type, and all samples oxidized considerably faster than HOPG at equivalent power. Birch wood (Braw) consistently ashed faster than all charcoals regardless of power, while the charcoals themselves also varied considerably in their response. Charcoal formed at 300°C consistently oxidized faster than charcoal formed at 600°C. The archaeological charcoals known to contain a considerable proportion of non-polyphenolic compounds (AZ and 73614) oxidized rapidly compared to other charcoal, while the effect of particle size on rate of oxidation in all samples was variable.

The carbon isotope composition of four charcoals (B300, B600, REU and HOSK) ashed for 1, 2 and 3 h at 25 W did not change appreciably, with the average difference between initial δ^{13}C value and δ^{13}C value after ashing being 0.18±0.11‰ (n=12), comparable with the analytical uncertainty (Table 2). The carbon content of these samples progressively decreased as ashing time increased, as a result of the relative increase in ash content accompanying the progressive oxidation of carbon in the charcoal.

3.2 radiocarbon dating

Radiocarbon analysis of the contaminated samples from Grotta di Fumane and Esquillieu returned ages within error of the previously measured ABA ages for the same samples and therefore substantially younger than the ABOx-SC age on the same material (Table 3). One aliquot of ashed Grotta di Fumane charcoal was also subjected to pre-combustion at 630°C prior to production of a graphite target from the residue. This marginally increased the age obtained, but still did not yield a result within error of the ABOx-SC date (Table 3). The dates on aliquots of the Esquilleu charcoal that were ashed for different lengths of time were indistinguishable from each other.

Two laboratory charcoal standards (Owen Buddleia and Maninjau) are routinely run at ORAU to monitor potential contamination introduced during pretreatment, and these standards were also processed concurrently with the samples from this study. The average results for Owen Buddleia after ABA (107.6±0.31 pMC, n=44) and ABOX-SC (107.7±0.31 and 107.5±0.29 pMC) indicate that no old carbon was preferentially introduced during either pretreatment. The average results for Maninjau after ABA (0.240+±0.047 pMC, n=16) and ABOX-SC (0.203±0.012 pMC, n=9) likewise indicates that neither pre-treatment preferentially introduces young contamination (Independent samples T test; t=1.547, df=23, p=0.136).

The results from these standards after plasma ashing of 107.8±0.30 pMC for Owen Buddleia and 0.207±0.025 pMC for Maninjau (Table 3) indicate that plasma ashing does not systematically introduce contaminant carbon of either younger or older age. As these standards were ashed together in the same run, this further suggests there is no cross-contamination of samples exposed together in the plasma chamber.

4. Discussion

4.1 plasma ashing

Figure 1 and the summary of all data presented in Figure 2 suggest that oxidation rate is a function of RF power applied to a sample, the chemical composition of the sample and to a lesser extent the surface area/particle size of the sample. The oxidation behaviour of an individual sample is both reproducible and controllable. These attributes mean that low-temperature plasma ashing has potential value as a technique for sample decontamination, and one where considerably more control over the effect of the pre-treatment on a sample can be exerted than is the case for wet chemical pre-treatments. Figure 3 demonstrates that the ashing process has negligible effect on the physical appearance of the sample, with the very fragile inorganic ash component remaining after complete removal of the carbon fraction retaining the original morphology of the sample.

It is clear that sample type does impact the rate of oxidation, suggesting that plasma ashing is to some extent selectively able to remove some materials from a mixed sample at a faster rate than others. In all cases the original ligno-cellulosic wood sample oxidized to 50% of its original mass at a rate 2-4 times faster than the slowest oxidizing charcoals at equivalent RF power, and all charcoal and wood samples oxidized considerably faster than HOPG at equivalent RF power. The observation that the low-temperature charcoal B300, along with the natural charcoals containing a high proportion of non-polyaromatic carbon (AZ and 73614), oxidize faster than the high temperature charcoal B600 at all powers, suggests that plasma ashing does selectively lead to the oxidation of some compounds more quickly than others.

Most oxidation profiles have a quasi-exponential form and the fact that this form is maintained when the 63-500 μm fraction is crushed to <63 μm suggests that the quasi-exponential nature of the oxidation profiles is not due simply to a particle size effect. Instead, the fact that the quasi-exponential shape is maintained when crushed but can lead to similar, higher or lower rates of oxidation than the 63-500 μm fraction provides further evidence that most samples are composed of at least two and probably many more components with different susceptibilities to plasma oxidation.

Differential rates of oxidation appear to be the norm even for charcoal samples such as B600 where NMR spectra suggest they are dominantly composed of aromatic carbon. This allows us to infer that most charcoal contains domains composed of more highly ordered oxidation-resistant 'graphitic' material within a matrix of less ordered polyaromatic carbon, as has been demonstrated in other studies (Cohen-Ofri et al., 2006, 2007). The fact that crushing to <63μm produces a different response in different samples may suggest that crushing variably exposes different components of the samples to plasma oxidation compared to the 63-500μm fraction of the same sample.

Results from a test of the ability of plasma ashing to differentiate between different compounds and particle sizes is shown in Figure 4. These results confirm the large difference in oxidation rate between birch wood and REU, with birch wood oxidizing very rapidly compared to REU. In addition, experiments with sucrose demonstrate that, oxidation was comparatively slow for the 63-500 μm fraction. This was most likely due to the absence of porosity in the surcose and hence a very low surface area compared to wood and charcoal. This conclusion is supported by the fact that the rate of oxidation increased dramatically when the sucrose was crushed to <63 μm. Fine-grained pure cellulose oxidized rapidly and linearly, with no dependence of oxidation rate on initial sample mass from 20-100 mg (Figure 4). Taken at face value the results in Figure 4 suggest that, after 100 mins at 25 W, if all surfaces were accessible to the plasma all labile non-charcoal material should be removed from a charcoal sample.

In order to further test the apparent selectivity of plasma ashing suggested by the above experiments, sample 73614, a charcoal known to contain a range of components as well as polyaromatic carbon, was ashed to varying degrees and then subjected to NMR analysis. Figure 5 demonstrates that while the intensity of peak assigned to aromatic carbon is progressively increased by plasma-ashing, a significant amount of other organic components remain present even after ashing to 23.4% of the original sample mass. In the NMR spectra from sample 73614, both unashed and ashed samples reveal contributions in both the regions for both aliphatic (0-115 ppm) and aromatic (115-190 ppm) carbons.

In the aromatic region, the broad signal is centred on 130 ppm, attributed to carbons within aromatic ring structures in charred plant materials, which increase in intensity during thermal degradation of plant biomass (Ascough et al., 2008). The signal in the aliphatic region relates to a variety of material. Between 0-50 ppm, aliphatic carbons, are represented by a broad, unresolved band (e.g. Mörck and Kringstad, 1985), and characteristic signal for lignin methoxyl groups, which increases with increased ashing time, is observed at 56 ppm (Hatcher et al., 1989). The peaks at 60-105 ppm are attributable to cellulose and hemicellulose, where carbons in the glucopyranose ring are visible at 72-75 ppm and 62-65 ppm, and remaining cellulose glycosidic bonds are revealed at ~105, 89 and 84 ppm (Atalla and Vanderhart, 1999; Earl and Vanderhart, 1981). It can be seen from Figure 5 that although the relative proportion of the aromatic signal increases in the spectra of ashed samples, the contribution from aliphatic carbons, though reduced, does not completely disappear.

This result suggests that, while in theory plasma ashing should be able to selectively remove compounds with different susceptibilities to oxidation, in practice this appears not to be the case. The reduced compound-selectivity of plasma ashing when applied to sample matrices that are heterogeneous at sub-micron scales is likely due to the fact that the technique is surface-specific, and therefore that even readily oxidisable compounds can only actually be oxidized once they are exposed at the surface of a particle.

4.2 radiocarbon dating

The radiocarbon dates presented in Table 3 suggest that plasma ashing and ABA pre-treatment yielded statistically indistinguishable ages and hence plasma ashing does not remove some contamination that is removed by the ABOx-SC technique. The addition of a pre-combustion step after plasma ashing, as applied in the ABOx-SC methodology, marginally increased the apparent age of one of the Grotta di Fumane samples (sample 20064.0) from 31,890±210 BP to 32,480±250 BP, but this date was still substantially younger than the ABOx-SC date on the same sample of 35,180±220 BP (Table 3). The analyses of the ORAU charcoal standards by ABA and ABOx-SC indicate that this difference cannot be due to 'old' contamination introduced during the ABOx-SC pretreatment.

As discussed above, the inability of plasma ashing to fully decontaminate charcoal is likely to be because it is a surface-active technique. Hence oxygen radicals are not able to penetrate significantly into the micropores that are characteristic of charcoal. Even crushing the samples prior to ashing was not sufficient to expose all contamination to the plasma. This is consistent with the NMR results (Figure 5), which suggest that plasma ashing is only weakly compound selective when applied to samples that are heterogeneous and porous at the sub-micron scale. The plasma must have direct access to all compounds to be selective and this is generally not possible even when samples are ground to <63 μm.

5. Conclusions

Low-temperature oxygen plasma ashing appears to hold promise as a controllable and reproducible alternative to wet chemical pre-treatments for radiocarbon dating of charcoal and potentially also of wood. The technique can certainly decontaminate charcoal samples as effectively as the conventional ABA pre-treatment, but does not appear to work as effectively as the ABOx-SC pre-treatment.

The technique could be used in place of the ABA pre-treatment that is used in most laboratories, with ashing complete in one to two h of unattended operation, for a total consumables cost of about one L of oxygen gas. Analysis of ancient and modern charcoal standards ashed in the same run demonstrates that there is no cross-contamination in the plasma chamber, and hence multiple samples can be ashed in a single run, providing further time savings.

An additional benefit of plasma ashing is that it minimizes sample handling, thus reducing sample loss during transfers and minimizing the opportunity for contamination to occur during handling. While the equipment investment is relatively costly (~USD$30,000), this would be recouped over time through savings on staff time. The protocol still requires an acid treatment to remove carbonates. However decarbonation can be achieved by exposure to HCl vapour (Cachier et al., 1989), making the treatment completely free of wet chemistry.

It seems likely that ligno-cellulosic and partly charred ligno-cellulosic material are more difficult to oxidize with a plasma discharge than other organic components owing to their cross-linked aromatic character. Hence the oxidation of labile compounds will be more rapid and ashing will serve to partly concentrate cross-linked aromatic components in the residue of ashing, but the technique is only weakly selective of bond types and compound classes. The failure of plasma ashing to isolate a purely poly-aromatic component from charcoal samples appears to be due to the highly surface-specificity of oxidation by oxygen radicals generated in the plasma. Thus, material physically protected within even finely crushed samples, including contaminant compounds, will not be exposed to the plasma and will remain after ashing. It is possible that complete decontamination may be possible by plasma ashing followed by stepped combustion, which would represent a significant saving in time over the ABOx-SC pre-treatment.

A major advantage of plasma ashing over both the ABA and ABOx-SC techniques is that it is controllable in terms of the rate of sample loss. This means that effective decontamination might be achievable through a fairly 'light-touch' ashing for small samples where wet chemical treatments may not leave sufficient material for analysis. Plasma ashing is appropriate where samples are not thought to be heavily contaminated and are expected to be younger than 25-30ka in age, where differences between ABA and ABOX-SC dates due to the presence of trace contaminants are less likely (Higham et al., 2009).

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References

Alon D., Mintz G., Cohen I., Weiner S. and Boaretto E., 2002. The use of Raman spectroscopy to monitor the removal of humic substances from charcoal: quality control for ^{14}C dating of charcoal Radiocarbon 44, 1-11.

Ascough, P., Bird, M.I., Wormald, P., Snape, C.E. and Apperley, D., 2008.. Influence of pyrolysis variables and starting material on charcoal stable isotopic and molecular characteristics. Geochimica et Cosmochimica Acta 72, 6090-6102.

Atalla R.H. and VanderHart D.L., 1999. The role of solid state 13C NMR spectroscopy in studies of the structure of native celluloses. Solid State Nuclear Magnetic Resonance 15, 1-19.

Baena, J., Carrión, E., Manzano, I., Veláquez, R., Sanz, E., Sánchez, S., Ruiz, B., Uzquiano, P., Yravedra, J. , 2005. 'Ocupaciones musterienses en la comarca de Liébana (occidente de Cantabria): la cueva de El Esquilleu' in M. Santonja, A. Pérezgonzalez, M. Machado (eds.), Geoarqueología y patrimonio en la Península Ibérica y el entorno mediterráneo, ADEMA, Almazán (Soria), 113-125.

Baena Preysler, J., Carrión Santafé, E., Velázquez Rayón, R., 2006. Tradición y coyuntura: claves sobre la variabilidad del Musteriense occidental a partir de la Cueva del Esquilleu' in Cabrera Valdés, V., Bernaldo de Quirós Guidotti, F., José Manuel Maíllo Fernández (eds.), En el centenario de la Cueva de El Castillo: El ocaso de los Neandertales, Madrid: Madrid: Ministerio de Educacion y Ciencia, 249-268.

Bird, M.I., 2006. radiocarbon dating of charcoal. In: Elias, S.A (editor) The Encyclopaedia of Quaternary Science. Elsevier, Amsterdam. 2950-2957.

Bird, M.I, Ayliffe, L.K., Fifield, L.K., Cresswell, R. and Turney, C., Barrows, T.T. and David, B., 1999. Radiocarbon dating of 'old' charcoal using a wet oxidation - stepped combustion procedure. Radiocarbon 41, 127-140.

Bird, M.I., Fifield, L.K., Santos, G.M., Beaumont, P.B, Zhou, Y., Di Tada, M.L. and Hausladen, P.A., 2003. Radiocarbon dating from 40-60ka BP at Border Cave, South Africa. Quaternary Science Reviews (Quaternary Geochronology) 22, 943-947

Bird, M.I., Turney, C.S.M., Fifield, L.K., Jones, R., Ayliffe, L.K., Palmer, A , Cresswell, R. and Robertson, S., 2002. Radiocarbon analysis of the early archaeological site of Nauwalabila I, Arnhem Land, Australia: implications for sample suitability and stratigraphic integrity. Quaternary Science Reviews 21, 1061-1075.

Brock, F. and Higham, T., 2009. AMS Radiocarbon Dating of Palaeolithic-aged charcoal from Europe and the Mediterranean Rim using ABOx-SC. Radiocarbon 51, 839-846.

Cachier H.P, Bremond M.P, Buat-Ménard P., 1989. Determination of atmospheric soot carbon by simple thermal method. Tellus 41B,379–390.

Church, M.J., Dugmore, A.J., Mairs, K-A., Millard, A.R., Cook, G.T., Sveinbjarnardóttir, G., Ascough, P.A., and Roucoux, K.H., 2007. Charcoal production during the Norse and early medieval periods in Eyjafjallahreppur, Southern Iceland. Radiocarbon 49, 659-672

Cohen-Ofri, I., Popovitz-Biro, R. and Weiner, S., 2007. Structural Characterization of Modern and Fossilized Charcoal Produced in Natural Fires as Determined by Using Electron Energy Loss Spectroscopy. Chemistry – A European Journal 13, 2306-2310.

Cohen-Ofri, I., Weiner, L., Boaretto, E., Mintz, G. and Weiner, S., 2006.. Modern and fossil charcoal: aspects of structure and diagenesis. Journal of Archaeological Science 33, 428-439.

Dai, X.J., 1996. Kinetic model of an RF discharge in Oxygen. Australian Journal of Physics 49, 1169-1180.

Earl, W. L. and VanderHart, D. L., 1981. Observations by high-resolution carbon-13 nuclear magnetic resonance of cellulose I related to morphology and crystal structure. Macromolecules 14, 570-574.

Gaudinski, J.B., Dawson, T.E., Quideau, S., Schuur, E.A.G., Roden, J.S., Trumbore, S.E., Sandquist, D.R., Oh, S.-W., and Wasylishen, R.E., 2005. Comparative analysis of cellulose preparation techniques for use with ^{13}C, ^{14}C and ^{18}O isotopic measurements. Analytical Chemistry 77, 7212–7224.

Hatcher P.G., Lerch, I., Harry, E., Bates, A.L. and Verheyen T.V., 1989. Solid-state 13C nuclear magnetic resonance studies of coalified gymnosperm xylem tissue from Australian brown coals. Organic Geochemistry 14, 145–155.

Higham T.F.G., Barton H., Turney C.S.M., Barker G., Bronk Ramsey C., Brock F. 2009. Radiocarbon dating of charcoal from tropical sequences: results from the Niah Great Cave, Sarawak, and their broader implications. Journal of Quaternary Science 24, 189-197.

Mörck R. and Kringstad K. P., 1985. 13C-NMR Spectra of Kraft lignins. Holzforschung 39, 109–119.

Rebollo, N.R., Cohen-Ofri, I., Popovitz-Biro, R., Bar-Yosef, O., Meignen, L., Goldberg, P., Weiner, S. and Boaretto, E., 2008. Structural characterisation of charcoal exposed to high and low pH; implications for ^{14}C sample preparation and charcoal preservation. Radiocarbon 50, 289-307.

Rowe, M.W. and Steelman, K.L., 2003. Comment on "some evidence of a date of first humans to arrive in Brazil". Journal of Archaeological Science 30, 1349-1351.

Russ, J., Hyman, M., Shafer, H.J. and Rowe, M.W., 1990. Radiocarbon dating of prehistoric rock paintings by selective oxidation of organic carbon. Nature 348, 710-711.

Santos, G.M. , Bird, M.I. , Pillans, B., Fifield, L.K., Alloway, B.V., Chappell, J. Hausladen, P.A. and Arneth, A., 2001. Radiocarbon dating of wood using different pretreatment procedures: application to the chronology of Rotoehu Ash, New Zealand. Proceedings of the 17th International radiocarbon Conference, Israel, June 18-23, 2000 Radiocarbon 43, 239-248.

Steelman, K.L., Rowe, M.W., Turpin, S.A., Guilderson, T. and Nightengale, L., 2004. Nondestructive radiocarbon dating: naturally mummified infant bundle from SW Texas. American Antiquity 69, 741–750.

Turney, C.S.M. Bird, M.I., Fifield, L.K., Roberts, R.G., Smith, M.A., Dortch, C.E., Grün, R., Lawson, E., Ayliffe, L.K., Miller, G.H., Dortch, J. and

Cresswell, R.G. and (2001. Breaking the radiocarbon barrier and early human occupation at Devil's Lair, southwestern Australia 50,000 years ago. Quaternary Research 55, 3-13.

De Vivo, B., Rolandi, G., Gans, P.B., Calvert, A., Bohrson, W.A., Spera, F.J. and Belkin, H.E.,, 2001. New constraints on the pyroclastic eruptive history of the Campanian volcanic Plain (Italy). Mineralogy and Petrology 73, 47-65.

Table captions:

Table 1. Characteristics and source of the samples used in plasma ashing tests to elucidate the controls on sample behaviour during ashing.

Table 2. Elemental and carbon isotope composition of selected samples ashed at 2 W for one to three h.

Table 3. Radiocarbon dates on samples analysed in this study. Sample numbers refer to different aliquots of the sample material dated after different pretreatments. ABOx-SC and ABA dates from Grotta di Fumane are from Brock and Higham (2009), while ABOx-SC and ABA dates from Esquillieu are unpublished (J. Maroto and J. Baena, pers. Commun.). All dates are quotes as radiocarbon years BP, corrected for δ^{13}C value, with ±1 σ errors except the Owen Buddleia and Maninjau charcoal standards which are quoted (italicized) as percent modern carbon (pMC). Proportion of mass lost during plasma ashing is provided in brackets. PA = plasma ashed; 'precombust' denotes sample subjected to precombustion for 2 hours at 630°C with CuO prior to final target preparation. OxA numbers denote dates that are produced from samples treated with routine chemistry and have passed quality assurance criteria. OxA-V numbers denote samples pre-treated outside of the ORAU laboratory.

Figure Captions:

Figure 1: Evolution of sample weight loss over time for particle sizes of <63 μm and 63-500 μm ashed using forward RF powers ranging from 2-100 W. Results are presented on an ash-free basis. Not all results for all samples are shown for reasons of clarity, and not all samples could be subjected to all treatments due to exhaustion of some samples.

Figure 2: Summary of data for the 63-500 μm fraction of all samples showing time taken to reduce the sample mass to 50% of the original mass (on an ash-free basis). This was calculated by interpolation between data points and does not represent a 'half-life' as sample mass loss is not exponential in most cases.

Figure 3: Scanning electron micrograph of B600 following complete ashing of carbon from the sample.

Figure 4: Weight loss profiles for REU and Braw at 25 W on an ash-free basis. Also shown are results for ashing fine (<63 μm) and coarse (63-500 μm) pure sucrose, and pure fine-grained (<2 μm) cellulose.

Figure 5: NMR spectra of charcoal sample 73614. A - spectrum for the sample prior to ashing; B - after ashing to 64.3% of original weight on an ash-free basis (10 W, 75 mins); C - after ashing to 23.4% of original weight on an ash-free basis (5 W, 1800 mins). Aromatic structures associated with polyaromatic compounds characteristic of charcoal are centred on 130 ppm.

Table 1

sample	sample description	%C	δ^{13}C (‰)	%ash
HOPG	Highly-ordered pyrolytic graphite (scitoys.com)	~100	-	<0.1
Braw	raw birch wood, Iceland	-	-	1.0

B300	300˚ laboratory-produced charcoal from birch wood, Iceland	66.3	-29.80	1.5
B600	600˚ laboratory-produced charcoal from birch wood, Iceland	81.2	-31.00	4.1
REU	archaeological birch charcoal, Iceland dated to 870AD±35yrs	54.2	-26.20	7.9
HOSK	archaeological birch charcoal, Iceland dated to 895AD±35yrs	55.0	-27.80	11.0
AZ	archaeological charcoal, species unknown, Faial Is., Azores ca. 2740BP	59.9	-22.71	3.0
73614	sub-recent charcoal, species unknown, Toca da Bastiana,Brazil	60.6	-26.55	3.6
Sucrose	Crystalline sucrose – unknown provenance	42.1	-	<0.1
Cellulose	Microcrystalline cellulose – unknown provenance	44.4	-	<0.1

Table 2

Sample-time	%C	$\delta^{13}C$
B300-1hr	66.0	-29.6
B300-2hr	59.2	-29.8
B300-3hr	47.6	-29.8
B600-1hr	83.3	-30.7
B600-2hr	80.0	-30.6
B600-3hr	73.1	-31.2
HOSK-1hr	57.0	-27.7
HOSK-2hr	54.7	-27.7
HOSK-3hr	47.0	-27.6
REU-1hr	54.8	-26.0
REU-2hr	53.0	-26.0
REU-3hr	45.4	-26.0

Table 3.

sample	Method	Site	%C	δ^{13}C	OxA	Date	+/-
22585.0	ABA	Esquilleu	60.0	-23.5	19085	39280	340
22585.1	ABOx-SC	“	62.9	-23.0	19086	58600	2600
22585.2	PA1 (42% ash)	“	52.3	-23.0	V-2284-29	39600	400
22585.3	PA2 (60% ash)	“	49.4	-23.0	V-2284-30	39650	450
13020.0	ABA	Grotta di Fumane	58.5	-25.2	11347	30650	260
20063.0	ABOx-SC	“	80.6	-22.5	17569	35640	220
20063.1	PA (33% ash)	“	58.4	-23.7	V-2284-7	31810	210
13021.0	ABA	Grotta di Fumane	44.3	-23.3	11360	31830	260
20064.0	ABOx-SC	“	74.5	-21.7	17570	35180	220
20064.1	PA (43% ash)	“	56.2	-22.7	V-2284-8	31890	210
20064.1	PA-precombust	“	83.7	-22.7	X-2298-8	32480	250
22844.3	PA (48% ash)	Owen Buddleia	75.1	-29.3	V-2284-10	*107.8*	*0.30*
22401.11	PA (61% ash)	Maninjau	84.8	-23.6	V-2284-17	*0.207*	*0.025*

Figure 1

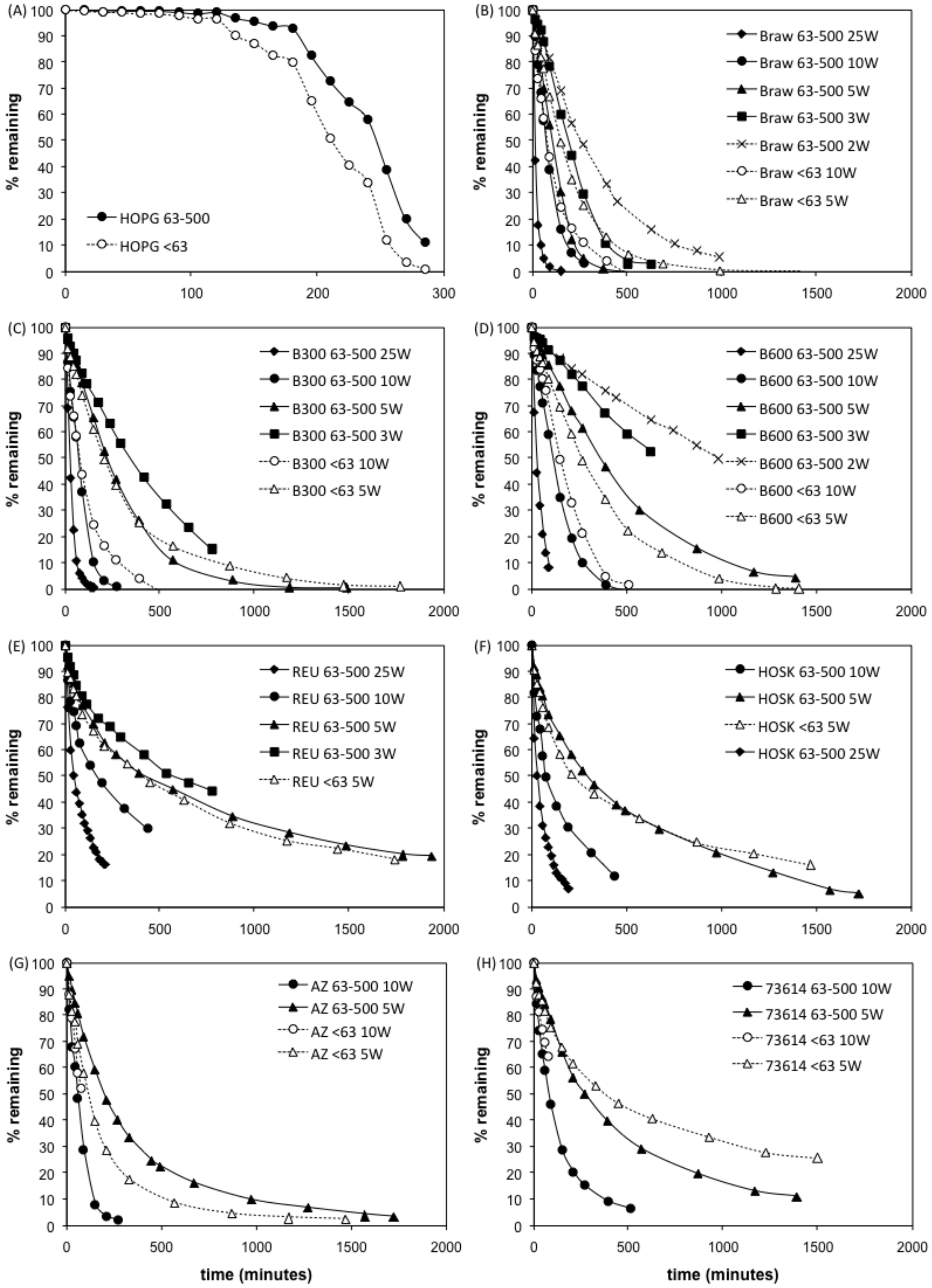
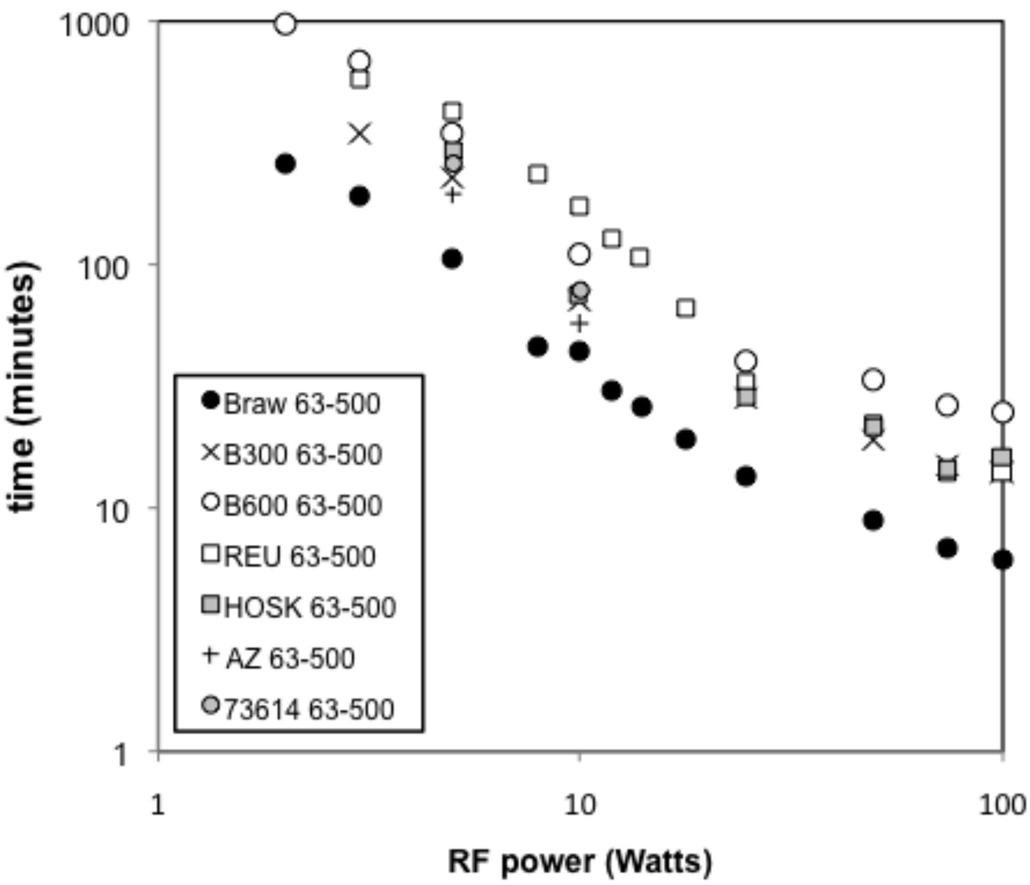

(A)
HOPG 63-500
HOPG <63
(B)
Braw 63-500 25W
Braw 63-500 10W
Braw 63-500 5W
Braw 63-500 3W
Braw 63-500 2W
Braw <63 10W
Braw <63 5W
(C)
B300 63-500 25W
B300 63-500 10W
B300 63-500 5W
B300 63-500 3W
B300 <63 10W
B300 <63 5W
(D)
B600 63-500 25W
B600 63-500 10W
B600 63-500 5W
B600 63-500 3W
B600 63-500 2W
B600 <63 10W
B600 <63 5W
(E)
REU 63-500 25W
REU 63-500 10W
REU 63-500 5W
REU 63-500 3W
REU <63 5W
(F)
HOSK 63-500 10W
HOSK 63-500 5W
HOSK <63 5W
HOSK 63-500 25W
(G)
AZ 63-500 10W
AZ 63-500 5W
AZ <63 10W
AZ <63 5W
(H)
73614 63-500 10W
73614 63-500 5W
73614 <63 10W
73614 <63 5W
% remaining
0
10
20
30
40
50
60
70
80
90
100
0
100
200
300
500
1000
1500
2000
time (minutes)

Figure 2



1000
100
10
1
time (minutes)
1
10
100
RF power (Watts)
Braw 63-500
B300 63-500
B600 63-500
REU 63-500
HOSK 63-500
AZ 63-500
73614 63-500

Figure 3

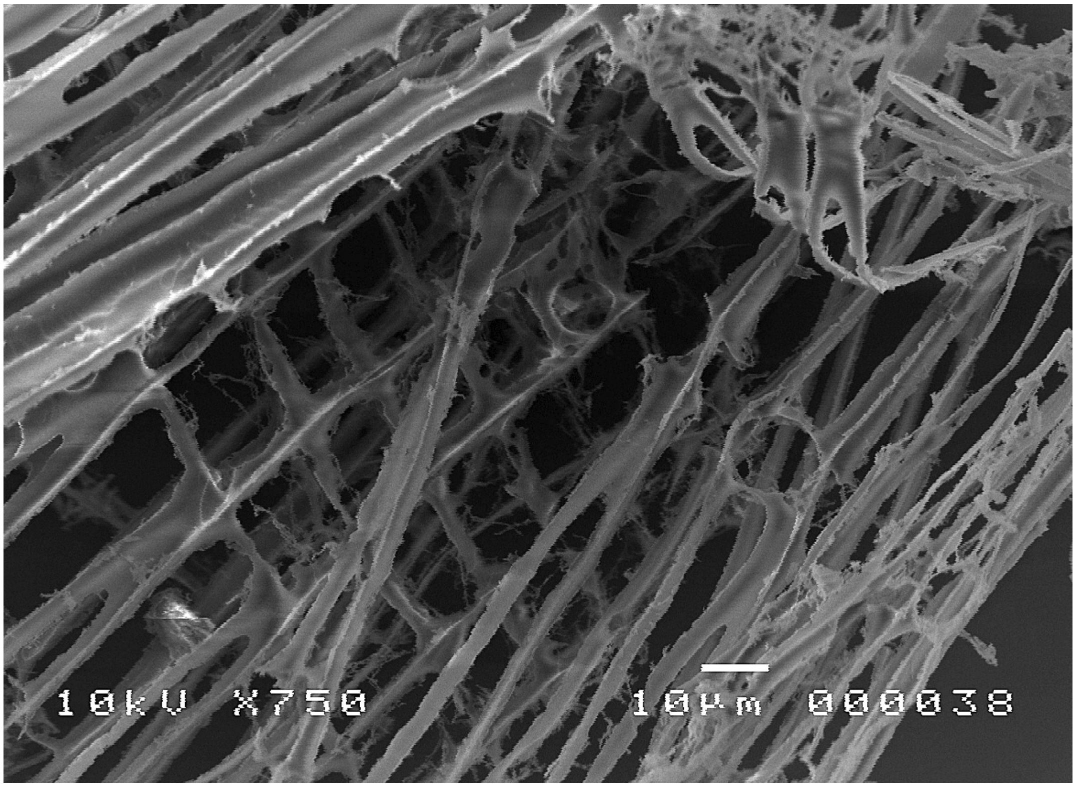


Figure 4

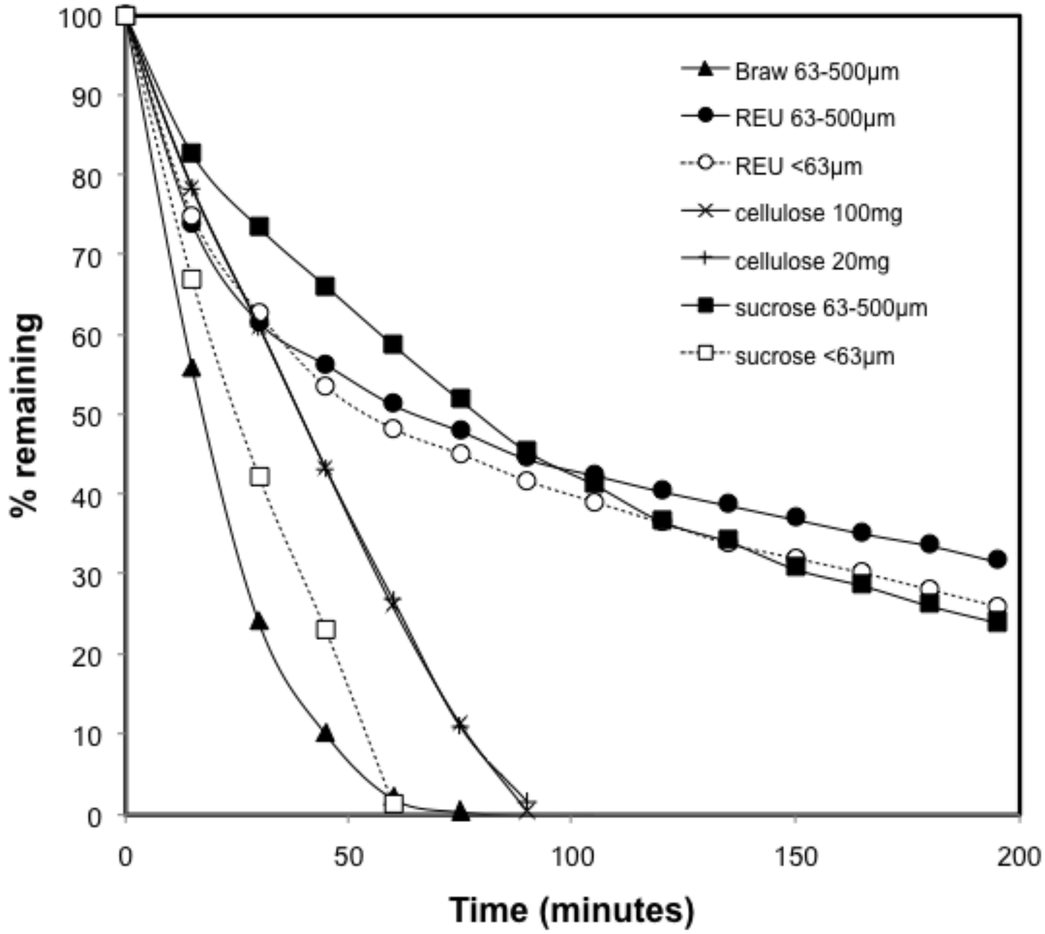

100
90
80
70
60
50
40
30
20
10
0
% remaining
0
50
100
150
200
Time (minutes)
Braw 63-500µm
REU 63-500µm
REU <63µm
cellulose 100mg
cellulose 20mg
sucrose 63-500µm
sucrose <63µm

Figure 5.