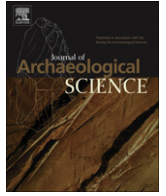


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Assessing natural variation and the effects of charring, burial and pre-treatment on the stable carbon and nitrogen isotope values of archaeobotanical cereals and pulses

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ABSTRACT

The aim of this study is to assess the potential of charred archaeobotanical cereal grain and pulse seed $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values to provide evidence of crop growing conditions and as a potential component of palaeodietary studies. In order to reliably interpret archaeobotanical $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values it is necessary to take into account the impact of charring, burial and laboratory pre-treatment procedures. We examine the effects of charring and burial on bulk $\delta^{13}\text{C}$, $\delta^{15}\text{N}$, %C, %N and C:N ratios in modern cereal and pulse material, and of cleaning by acid–base–acid (ABA) pre-treatment on modern and archaeobotanical charred material. Our study utilised bulk grain and seed samples to help account for within-ear/pod and between-plant variability in $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values. Heating at relatively low temperatures and for prolonged times (230 °C for up to 24 h) is conducive to the formation of well preserved, undistorted charred cereal grain and pulse seed. Heating for 24 h has a systematic and predictable effect on $\delta^{15}\text{N}$ values, with increases of around 1‰ on average in cereal grains and pulse seeds, and no consistent impact on $\delta^{13}\text{C}$ values. Increases in $\delta^{15}\text{N}$ are likely due to the loss of lighter ^{14}N via N-containing volatiles. Burial (for up to 2 years) and ABA pre-treatment have no significant effects on $\delta^{13}\text{C}$ or $\delta^{15}\text{N}$ values. After pre-treatment, however, the %C and %N contents of the archaeobotanical material more closely resembles that of the modern charred grains and seeds, suggesting that archaeobotanical remains accumulate non-structural material during burial but retain their original carbon and nitrogen content. Therefore %C, %N contents and C:N ratios can provide useful criteria for assessing archaeobotanical preservation.

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1. Introduction

The charred remains of seed crops, especially cereals and pulses, form a large component of the Eurasian archaeobotanical record from the later prehistoric period onwards and provide evidence of plant use and consumption (e.g. Dennell, 1976; Jacomet and Kreuz, 1999). Associated weed evidence offers further valuable information about farming practices and land management (e.g. Jones et al., 2000). More recently, the stable carbon and nitrogen isotope analysis of crops has been explored as a means of obtaining *direct* and complementary evidence of crop growing conditions. Carbon isotope values ($\delta^{13}\text{C}$) of cereal crop

remains have mainly been used to explore water management regimes, and to a lesser extent changes in local precipitation/moisture and climate conditions (Ferrio et al., 2005, 2006, 2007; Fiorentino et al., 2008; Riehl, 2008; Riehl et al., 2008; Voltas et al., 2008; Heaton et al., 2009; Roberts et al., 2011; Wallace et al. in prep). Nitrogen isotope values ($\delta^{15}\text{N}$) have been shown to be a useful tool to identify land-use practices such as manuring and associated changes in soil productivity as the nitrogen cycle changes with human intervention (Bogaard et al., 2007; Aguilera et al., 2008; Fraser et al., 2011). In palaeodiet studies the stable isotope values of plant-diet components are usually the ‘unknown factors’ and their values are estimated by subtracting trophic level diet to bone collagen fractionation values (usually +3 to +5‰) from the collagen isotope values of herbivores. The addition of actual plant-diet *food* isotope values to dietary models can potentially refine palaeodietary reconstructions.

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In order to reliably interpret archaeobotanical crop stable isotope values it is necessary to take the impact of preservation processes and burial conditions into account. The depositional contexts of crop remains can vary from concentrated storage deposits to middens where sweepings from cooking hearths and crop processing areas accumulated (van der Veen, 2007). Buried grain and seeds are thus variously exposed to potential contaminants and diagenesis in soil, where original molecules can be removed or replaced by microbes or infiltrating groundwater. The crop remains retrieved from archaeological sites are often preserved by charring or carbonisation, a condition that involves heating but not combustion. The charring processes are assumed responsible for preserving many of the original biomolecules in ancient plant remains and rendering them less susceptible to degradation and microbial attack (Knicker et al., 1996; Almendros and Dorado, 1999). It is widely recognised that charring can affect the morphology (e.g. size and shape) of crop remains (Boardman and Jones, 1990; Braadbaart and van Bergen, 2005; Braadbaart, 2008; Märkle and Rösch, 2008), but the effects of charring on cereal and pulse crop bulk $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values have not been explored in detail. In addition, the isotope effects of burial in soil have rarely been tested under experimental conditions.

Chemical pre-treatment of ancient plant material and charcoal prior to $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ analysis is considered necessary to remove exogenous carbonates deposited from groundwater and humic acids (Kelly et al., 1998; Fernandes and Krull, 2008; Ascough et al., 2010a). The Acid–Base–Acid (ABA, see Section 2.5) pre-treatment technique is routinely applied to charred plant remains undergoing radiocarbon dating (Higham et al., 2009) and is considered essential to remove non-structural and exogenous younger radiogenic ^{14}C because even a small amount of contamination can result in incorrect dates (Taylor, 1987). However, effects on $\delta^{13}\text{C}$ values are of less concern for radiocarbon dating and little is known about the effects of the ABA pre-treatment on the nitrogen that remains in ancient charred plant materials.

In this study we consider three main areas of stable isotope investigation. First, we examine the effects of charring, under a set of conditions conducive to the optimal preservation of morphologically intact, undistorted cereal grains and pulse seeds, in a set of Eurasian crops. Secondly, we examine post-depositional effects through burial of charred crop remains in garden soil and submersion in humic acid solution. Thirdly, we examine the effects of the ABA pre-treatment as a cleaning method. Overall, we seek to identify if there are systematic and significant changes in bulk $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values, as well as percentage carbon and nitrogen content and resulting C:N ratios, arising from any of these factors. It is also necessary to take natural variation in the stable isotope values of crops grown under standardized conditions into account. This assessment can help with determining adequate sample sizes and identifying meaningful differences in isotope values among samples. We report on the magnitude of stable isotope variations (from two associated studies – Bogaard et al., 2007; Fraser et al., 2011) observed in grains and seeds from a single plant and in different plants grown on the same experimental field/plot and discuss how these variations may influence our interpretations. In this paper we focus principally on the effects that are detectable at the bulk stable isotope level because these analyses are commonly used and interpreted in archaeological science. Solid state ^{13}C NMR and FT-IR techniques examining the molecular composition of modern and archaeological charred crop remains to assess molecular changes due to charring, post-depositional preservation and ABA pre-treatment are investigated by Styring et al. (this volume) in conjunction with our studies.

2. Background: stable isotopes and preservation of charred plant remains

DeNiro and Hastorf (1985) drew attention to the ‘effects of charring’ as a necessary precursor for preserving the isotopic signatures of archaeobotanical remains; this was because the $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values of uncharred (desiccated) plants (many of which were edible legumes, seeds and fruits), in contrast to charred plants, were highly variable and differed considerably from their modern counterparts (e.g. 8–21‰ for $\delta^{15}\text{N}$). Another early study (Marino and Deniro, 1987) observed that the effects of various cooking procedures, one of which included carbonization, indicated negligible effects on $\delta^{13}\text{C}$, $\delta^{18}\text{O}$ and δD values of plant cellulose; on this basis, the authors suggested that there is potential for obtaining ‘palaeoclimatic’ information from either cooked or uncooked plant remains. A substantial amount of research relevant to our study has been undertaken on the isotopic effects of heating and charring of wood, grasses and leaves (Turekian et al., 1998; Czimczik et al., 2002; Turney et al., 2006; Bird and Ascough, 2012). These studies focus mainly on the changes in $\delta^{13}\text{C}$ values rather than $\delta^{15}\text{N}$ values. While contradictory and highly variable effects have been observed, the magnitude of change in plant tissue $\delta^{13}\text{C}$ values due to charring have mostly been in the range of 1–3‰ (Turekian et al., 1998; Czimczik et al., 2002; Turney et al., 2006; Ascough et al., 2008).

The preservation potential and $\delta^{13}\text{C}$ isotope composition of charred wood are recognised as being the result of a complex set of parameters, including charring temperatures and times, aerobic or anaerobic conditions, soil pH and microbial or fungal attack, and also the initial composition (e.g. proportions of cellulose and lignin) (Czimczik et al., 2002; Ascough et al., 2008, 2010b). Wood charcoal studies provide highly relevant background to the charring of crop remains studied here, but the biochemical composition and physical structures of cereal grains and pulse seeds vary significantly from wood. Wood is comprised predominantly of ~65–75% carbohydrates (~35–40% cellulose and ~25–35% hemicelluloses), ~18–28% lignin and the remainder are ~4–10% organic extractives, which can include compounds such as lipids, waxes, alkaloids, proteins, phenolics, simple sugars, starches and essential oils (Pettersen, 1984). In contrast, cereal grains and pulse seeds are composed of negligible lignin or cellulose (some in the outer epidermis), many polysaccharides (with ~60% starch), smaller amounts of proteins (~3–8%) and very low amounts of lipids (~2%) (Braadbaart et al., 2004a). For this reason, the effects of charring and preservation specific to crop remains warrant more investigation.

The changes in plant $\delta^{13}\text{C}$ values observed due to heating can be influenced by the different stable isotope compositions of individual biochemical components, such as lipids, lignins, carbohydrates and proteins. Differences in the $\delta^{13}\text{C}$ values of these components can depend on the plant species and the tissues analysed. For example, lignin can be ~1‰ lower than and cellulose ~2‰ higher than bulk wood $\delta^{13}\text{C}$ values (O’Leary, 1981; Benner et al., 1987; Tieszen, 1991; Loader et al., 2003). The lipid components show the greatest differences; $\delta^{13}\text{C}$ values can be ~3–8‰ lower than bulk plant $\delta^{13}\text{C}$ values (Park and Epstein, 1961). It follows that preferential losses or changes in a biochemical component over another during charring may significantly change the final bulk isotope value of the material.

Archaeological studies that have concentrated on the isotope effects of cooking or charring of plants have focused mainly on pot residues (Hart et al., 2007, 2009; Boyd et al., 2008), and it is acknowledged that little experimental stable isotope research has been done on actual crop/plant–food remains themselves (Dürwächter et al., 2006; Bogaard et al., 2007). The work of Arous

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