

Carbon isotope fractionation in wood during carbonization

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Abstract

A significant uncertainty exists as to whether $\delta^{13}\text{C}$ values in charcoal meaningfully represent the stable isotopic content of the original material, with studies suggesting variable responses to both natural and laboratory heating. An extensive study was undertaken using fully homogenised samples of wood taken from *Eucalyptus* spp., *Quercus robur* and *Pinus radiata*. The results demonstrate that the duration of heating had no tangible effect on the final composition of the charred material, with the $\delta^{13}\text{C}$ and carbon content of wood fixed after 30 min of heating. Furthermore, all three wood types become progressively depleted in ^{13}C with increasing temperature. The results demonstrate that even at temperatures commonly reached in natural fires (<450 °C) isotopic fractionation of up to 1.3‰ can take place indicating that the absolute values obtained from charcoal extracted for paleoenvironmental reconstruction must be interpreted with caution.

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1. Introduction

Numerous studies of charcoal in sedimentary sequences have helped elucidate biogeochemical processes across a range of different temporal and spatial scales. For instance, naturally produced charcoal is a major product of biomass burning and may be recalcitrant in soils, potentially playing a significant role as a global carbon sink (Kuhlbusch, 1998; Bird et al., 1999). Although significant advances have been made in understanding the broad processes of charcoal formation and its preservation in sediments (e.g., Ballentine et al., 1998; Baldock and Smernik, 2002; Harden et al., 2004; Janssens, 2004), some key processes and mechanisms remain inadequately explained. Of particular concern is the uncertainty regarding the magnitude of ^{13}C fractionation relative to ^{12}C ($\delta^{13}\text{C}$) during carbonization, despite the important implication this has for the interpretation of stable isotopic values within charcoals. For instance, if measuring $\delta^{13}\text{C}$ in finely disseminated sedimentary charcoal to reconstruct changes in C3/C4 abundance (assuming values of -26‰ and -12‰ for C3 and C4 plants, respectively), a 1‰ fractionation would im-

ply a 7% error in the reconstruction of their relative abundance.

Numerous studies have demonstrated that the $\delta^{13}\text{C}$ of plant material is a measure of the environmental conditions under which the tissues formed (e.g., Ehleringer and Cooper, 1988; Farquhar et al., 1989; Turney et al., 1999, 2002). As a result, sedimentary charcoal and its $\delta^{13}\text{C}$ have been used to reconstruct paleoclimatic, paleoenvironmental and archaeological changes (Hopkins et al., 1993; Turney et al., 2001a,b). Many stable isotopic studies assume that the $\delta^{13}\text{C}$ preserved in naturally occurring charcoal directly represents the vegetation from which it is derived, implying a negligible or constant fractionation regardless of the temperature at which the sample formed. This is assumed despite the fact that organic plant matter is made up of a host of different components, each with their own distinct isotopic signature. These include refractory compounds such as lignins, which are relatively ^{13}C depleted, and more oxidisable ('labile') compounds such as holo-cellulose that have a higher ^{13}C content (Nadelhoffer and Fry, 1988). Natural surface fires can range from <300 to >1000 °C (Braithwaite and Estbergs, 1985; Whelan, 1995) and these would be expected to generate different stable carbon isotopic shifts in wood during charring as a result of the variable thermal tolerances of the above compounds.

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Several attempts have been made to quantify the extent to which the carbon isotopic content of wood fractionates during the process of carbonization. Previously published results are contradictory, indicating an enrichment in ^{13}C content (Turekian et al., 1998), a depletion in ^{13}C (Bird and Gröcke, 1997; Czimczik et al., 2002) and no change in the stable isotopic content (Schleser et al., 1999). Moreover, Leavitt et al. (1982) have raised the possibility that experimental charring (under vacuum) results in different isotopic values to those produced naturally, possibly as a result of the bathing of wood in flames and gases, differences in surface area, or variations in temperature. Within these studies no attempt has been made to identify whether charring during different periods at the same temperature can cause variable $\delta^{13}\text{C}$ values. Recently, a comprehensive study by Krull et al. (2003) reported a range of charring experiments under natural and laboratory conditions that produced different isotopic fractionation trends with different sample types, but it was unclear whether there was any systematic change during different temperature regimes. This is surprising given that kinetic isotope effects should be independent of the nature of the unburned plant material (Ballentine et al., 1998). Although apparently extensive, it is unclear to what extent samples had been homogenised in the Krull et al. study prior to charring. If confirmed, however, such results have important implications for palaeo studies.

As a result of the above, the following study was undertaken to address three key questions:

1. Do the carbon content and isotopic characteristics of wood remain the same regardless of the duration of charring?
2. Is there any carbon isotope fractionation associated with heating at different temperatures?
3. Is there any difference in the carbon isotopic values obtained from laboratory- and naturally produced charcoal?

2. Methods

Three different wood types were selected for this study: *Eucalyptus* spp, *Quercus robur* and *Pinus radiata*. Wood samples from six years of growth rings were chipped and homogenised thoroughly in a Tema (chrome steel) mill where they were crushed for two periods totalling 80 s. 1–3 g of the different wood types were then subsampled. To minimise air contact of the samples and create charring conditions, the samples were double wrapped in aluminium foil packets and tightly folded. Individual packets of samples were then placed within a muffle furnace preheated to 200, 400, 600 or 800 °C for periods of 30, 60, 120 or 240 min. As soon as the period was completed, the samples were immediately removed from the furnace. In addition, subsamples were also heated on a metal aluminium foil tray over a heat gun set to 350 °C to simulate natural

smouldering under oxygenated conditions. This was undertaken until all the material had visibly charred. The sample was constantly stirred during this process to prevent the build up of ash.

Pre-charred and charred wood samples were all then ground using a pestle and mortar prior to analysis. Between 1 and 5 mg of sample was weighed into tin capsules for automated combustion in an NA 1500-NCS III elemental analyser interfaced to a continuous flow VG Prism isotope ratio mass spectrometer in the School of Earth and Environmental Sciences at the University of Wollongong. The carbon dioxide gas evolved was resolved using chromatographic separation on a GC column at 40 °C, and analysed for isotopic abundance. Standards and blanks were included during the run for internal calibration. $\delta^{13}\text{C}$ values are reported as per mille (‰) relative to V-PDB. Analytical precision for $\delta^{13}\text{C}$ at the 1σ level is reported as 0.15‰. Duplicate measurements were made of all samples, except the pre-charred samples of which four measurements were made.

3. Results and discussion

The values obtained from the charred material indicate that regardless of the duration of heating at one temperature, the carbon isotopic and content of wood does not vary significantly (Table 1). In all instances, the values obtained following 30 min of heating were virtually identical to that of 240 min, indicating that the chemical composition of the charred wood during carbonization become fixed within the first 30 min of heating and that subsequent periods have negligible influence on the charcoal. The greatest changes experienced were by *Q. robur* where the $\delta^{13}\text{C}$ shift during the course of heating was 1.2‰ at 400 °C while the largest shift in carbon content were recorded by *P. radiata* which experienced a range of 20% at 400 °C. In *Eucalyptus* spp., the maximum change the wood experienced during increasing durations of heating from 30 to 240 min was 0.7‰ for $\delta^{13}\text{C}$ (at 400 °C), while the carbon content varied by 14% (at 600 °C). Generally, however, changes were significantly less, with $\delta^{13}\text{C}$ of 0.3‰ and carbon content variations of <10% typically recorded across the different durations of heating at a set temperature. In virtually all instances, the changes in content were not linear with time but varied around the mean. The $\delta^{13}\text{C}$ values obtained in this study range from –24.5‰ to –28.1‰ and fall within charcoal values reported previously in the literature (–10.5‰ to –30.8‰) (Burleigh et al., 1984).

Progressively increasing organic carbon content of the charcoal samples with increasing charring temperatures indicates that flaming and complete combustion under oxygenated conditions (with the associated formation of ash) did not take place (Table 1). The exception to this was during heating at 800 °C for over 30 min where all of the wood samples combusted as a result of the disintegration of the aluminium foil.

Table 1
Summary $\delta^{13}\text{C}$, carbon content and mass remaining of *Eucalyptus* spp., *Quercus robur* and *Pinus radiata* wood samples heated at different temperatures and durations

Temperature (°C)	Heating period (min)	Sample No.	<i>Eucalyptus</i> spp.				<i>Quercus robur</i>				<i>Pinus radiata</i>				
			% C	$\delta^{13}\text{C}$ (‰)	$\Delta\delta^{13}\text{C}$ (‰)	% Mass left	% C	$\delta^{13}\text{C}$ (‰)	$\Delta\delta^{13}\text{C}$ (‰)	% Mass left	% C	$\delta^{13}\text{C}$ (‰)	$\Delta\delta^{13}\text{C}$ (‰)	% Mass left	
25		1	47.5	-26.5			46.6	-25.6			52.8	-25.1			
		2	43.3	-26.3			43.4	-26.0			41.9	-24.7			
		3	48.6	-26.2			47.4	-25.6			44.9	-24.6			
		4	46.7	-26.4			46.8	-25.6			48.5	-24.7			
		Mean	46.5	-26.4			46.1	-25.7			47.0	-24.8			
200	30	1	53.3	-26.6		82.1	52.4	-25.9		79.7	40.1	-24.5		90.8	
		2	51.4	-26.8			46.8	-25.7			46.2	-24.6			
	60	1	54.4	-26.4		79.6	48.5	-25.9		83.0	47.2	-24.9		90.4	
		2	51.7	-26.6			48.8	-25.7			49.1	-24.7			
	120	1	51.7	-26.7		80.6	51.5	-25.7		74.8	49.2	-25.0		89.1	
		2	48.9	-26.5			53.9	-25.8			43.6	-24.9			
	240	1	42.5	-26.6		77.4	50.3	-25.7		76.9	42.0	-24.8		88.9	
		2	47.0	-26.5			50.1	-25.7			46.3	-24.8			
		Mean	50.1	-26.6	-0.2	79.9	50.3	-25.8	-0.1	78.6	45.5	-24.8	0.0	89.8	
	400	30	1	77.0	-27.7		29.3	66.9	-26.0		31.9	68.2	-25.9		29.1
			2	74.0	-27.7			88.9	-26.4			69.0	-25.9		
		60	1	78.7	-27.2		37.9	73.9	-26.6		30.2	65.6	-25.4		37.4
2			70.3	-27.6			73.8	-26.6			71.6	-25.8			
120		1	71.8	-27.7		30.9	71.0	-26.8		27.1	57.7	-26.2		26.3	
		2	74.9	-27.6			76.8	-26.9			56.7	-25.9			
240		1	76.2	-27.9		27.6	78.1	-26.9		21.8	76.7	-26.2		21.0	
		2	76.9	-27.8			84.3	-27.2			77.1	-26.1			
		Mean	75.0	-27.7	-1.3	31.4	76.7	-26.7	-1.0	27.8	67.8	-25.9	-1.1	28.5	
600		30	1	85.4	-27.9		22.6	84.9	-27.1		20.1	97.6	-26.6		16.3
			2	83.1	-28.1			82.3	-26.9			85.4	-26.6		
		60	1	95.7	-27.9		21.7	98.9	-27.1		19.7	84.3	-26.5		17.5
	2		91.6	-28.2			93.4	-27.0			92.8	-26.4			
	120	1	89.8	-28.1		20.2	94.3	-27.3		16.3	82.5	-26.7		16.3	
		2	95.0	-28.1			87.4	-27.2			88.4	-26.7			
	240	1	91.5	-28.0		20.0	86.9	-27.2		14.3	92.3	-26.4		11.4	
		2	97.8	-27.9			91.5	-27.2			91.1	-26.4			
		Mean	91.2	-28.0	-1.6	21.1	90.0	-27.1	-1.4	17.6	89.3	-26.5	-1.7	15.4	
	800	30	1	89.4	-27.9		12.8	87.8	-26.7		11.6	87.2	-26.7		10.4
			2	90.7	-27.8			90.1	-26.9			93.7	-26.6		
			Mean	90.1	-27.9	-1.5	(12.8)	89.0	-26.8	-1.1	(11.6)	90.5	-26.8	-2.0	(10.4)
Air 350 °C		1	54.7	-26.7		53.9	62.1	-26.1		37.6	56.2	-25.2		51.0	
		2	56.5	-26.6			61.4	-26.2			61.6	-25.3			
		Mean	55.6	-26.7	-0.3	(53.9)	61.8	-26.2	-0.4	(37.6)	58.9	-25.3	-0.4	(51.0)	

$\Delta\delta^{13}\text{C}$ defines difference between mean charred and original (pre-charred) isotopic values.

Although in natural contexts wood is inherently heterogeneous at different scales, the analyses undertaken here under laboratory conditions do provide a quantification of the processes that can operate during carbonization. Overall, the $\delta^{13}\text{C}$ values obtained from the different wood types indicate that although the duration of heating had a negligible influence, increasing temperature had a systematic effect on the final character of the remaining material, regardless of the wood type (Fig. 1 and Table 1) in contrast to the results reported by Krull et al. (2003). In *Eucalyptus* spp. and *Q. robur* $\delta^{13}\text{C}$ values appear to remain complacent above 600 °C, stabilising at differences of around 1.6‰ and 1.4‰ relative to the original wood samples respectively. In *P. radiata*, although carbon isotopic fractionation appears to have continued to increase up to 800 °C, with a mean

discrimination of 2‰ compared to the unheated pre-charred wood sample, the two values recorded at this temperature do form part of the range obtained at 600 °C, suggesting little $\delta^{13}\text{C}$ change. Overall, the stable isotopic content shifted progressively with increasing temperature for all samples (Fig. 1), with a relative depletion in the ^{13}C content of wood, supporting earlier observations (Bird and Gröcke, 1997; Czimczik et al., 2002). In contrast with earlier studies, however, the fractionation identified here increased with temperatures up to at least 600 °C.

Following initial carbon fixation as a result of photosynthetic gas exchange, secondary metabolism by plants results in further kinetic isotopic effects, making lignin relatively more ^{13}C depleted compared to cellulose and bulk organic matter by 1–7‰ (Benner et al., 1987; Loader

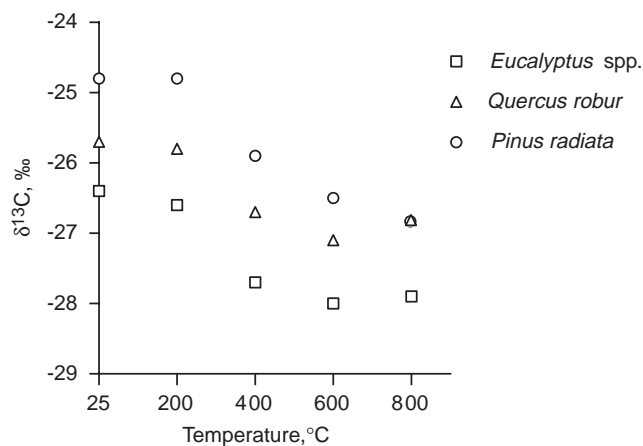


Fig. 1. Mean $\delta^{13}\text{C}$ values for *Eucalyptus* spp., *Quercus robur* and *Pinus radiata* wood samples heated in a muffle furnace at different temperatures.

et al., 2003). The results presented here are consistent with various workers (Baldock and Smernik, 2002; Czimeczik et al., 2002; Harden et al., 2004) who suggested that during the carbonization process, thermally labile carbon compounds are more likely to become lost, with a relative enrichment in lignin-like compounds, ultimately resulting in a ^{13}C -depleted content. The observed shifts in this study coincide with changes in the mass of wood remaining (Table 1), with between 80% and 85% mass loss at 600 °C, consistent with the greater susceptibility of cellulose to thermal degradation relative to lignin (Czimeczik et al., 2002). At temperatures greater than 600 °C, mass loss approaches 90% with little shift in $\delta^{13}\text{C}$ values, suggesting similar susceptibility to thermal degradation of both components.

Convincingly, even where heating takes place in a fully oxygenated environment, such as undertaken during smouldering at approximately 350 °C, the $\delta^{13}\text{C}$ values are intermediate between those obtained at 200 and 400 °C from heating in aluminium foil parcels within a muffle furnace (Table 1) with a depletion in ^{13}C of 0.3–0.4‰. The positioning of the isotopic results from smouldering at 350 °C fall almost directly on the inferred trend derived from muffle-furnace charring (Fig. 1), suggesting that no significant bias exists between laboratory and natural heating.

The above observation conflicts with the major discrepancy reported between natural and laboratory-produced charcoal (Leavitt et al., 1982). Differences in surface area can be discounted because the sample size was identical between the muffle furnace and smouldering heated samples. Intriguingly, the degree of fractionation associated with smouldering (0.3–0.4‰) is comparable to the 0.3‰ identified by Leavitt et al. (1982) from a sample of *Juniperus* spp. wood heated within a fireplace, although the temperature at which the latter was obtained is unreported. The latter fractionation in absolute terms, however, was significantly lower than that observed during heating of the same wood type under vacuum where a maximum shift of 2.4‰ was observed at 300 °C, above which temperature the isotopic

values remained constant. It seems probable that when heating wood under vacuum, the ^{13}C -enriched organic components (such as cellulose) are more rapidly lost at relatively lower temperatures than during heating under natural conditions (such as mimicked here in the muffle furnace). As a result, the fractionation effect is accelerated under vacuum at a considerably lower temperature than during natural charring conditions, creating a marked difference in the trends between differently produced charcoal $\delta^{13}\text{C}$ values.

The linear relationship between heating and isotopic fractionation raises the intriguing possibility that if charred and pre-charred wood can be obtained from stratigraphically constrained units, it may be possible to reconstruct past burn temperatures up to 600 °C. Furthermore, for palaeoenvironmental reconstructions, even at temperatures typically found in the natural occurring fires at <450 °C (Whelan, 1995), significant isotopic fractionation takes place. All samples demonstrated that even at 400 °C, a shift in $\delta^{13}\text{C}$ of between 1.0‰ and 1.3‰ took place. As a result, this raises significant questions regarding the use of absolute carbon isotopic values in charcoal samples extracted from sedimentary sequences unless the temperature at which burning took place is known. If the burn temperature is not known, a correction of 1‰ may go some way to improving the estimate of the original isotopic composition of the plant material.

4. Conclusions

The extent to which the stable carbon isotopic content of wood fractionates during carbonization is unclear from previous studies that have suggested a range of different changes in ^{13}C content following heating. Within this study, different wood samples were exposed to a range of heating temperatures and measured for their $\delta^{13}\text{C}$ and carbon content. The results demonstrate that the carbon content and isotopic values do not vary with the duration of heating at a set temperature. Significant isotopic fractionation, however, does take place during progressive heating with isotopic depletion in ^{13}C by up to 1.3‰ recorded for temperatures typically reached in naturally occurring fires (<450 °C). The use of absolute $\delta^{13}\text{C}$ values obtained from sedimentary charcoal for reconstructions of palaeoenvironmental and paleoclimatic change should therefore be interpreted with caution. A correction of around 1‰ may help to improve the estimate of the stable carbon isotopic composition of the original plant material if no estimate of the burning temperature can be obtained.

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