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MASS SPECTROMETRIC STUDIES OF CARBON 13 VARIATIONS IN CORN AND OTHER GRASSES

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Our experience in radiocarbon dating has shown that dates obtained from samples of corn cob and kernels are usually too young compared with dates from wood samples. Since other laboratories have also commented on the same problem, a study of C^{13}/C^{12} ratios in corn and other plant materials has been undertaken.

The fact that all plants discriminate against C^{13} in photosynthesis has been well documented (Wickman, 1952, Craig, 1953 and 1954). The range for δC^{13} relative to the Pee Dee belemnite (PDB) standard of the Univ. of Chicago has been established as -20 to $-30‰$, an average of $-25‰$, for wood and most terrestrial plant materials. Mass spectrometric analyses of corn cob and kernels have, however, shown a range of -10 to $-12‰$ (Stuiver and Deevey, 1962, Hall, 1967a and 1967b, Tauber, 1967), and some grasses have shown δC^{13} values of the same magnitude (Craig, 1954, Hall, 1967b, Tauber, 1967). This anomalous enrichment in the heavy isotope of carbon in corn relative to wood has usually been attributed to the release of carbon dioxide from limestone soils or to differences in microclimatic conditions. Carbon dioxide from ancient limestone soils should, however, make the radiocarbon age too old rather than too young.

Both modern and prehistoric corn samples, *Zea mays*, from a variety of locations have been analyzed and the C^{13}/C^{12} ratio has been found to be approximately constant (Table 1). These results are in agreement with the C^{13}/C^{12} values reported by other laboratories. Other grains and grasses grown on limestone soil adjacent to the corn were analyzed and it was found that soybeans, wheat, barley, timothy, and oats all had δC^{13} values in the same range as wood, -26.9 to $-28.2‰$ (Table 2). There was no apparent effect from limestone soil. One group of grasses, however, showed a consistent enrichment in C^{13} with δC^{13} similar to the corn; tropical grasses such as Sorghum, Sudan grass, sugarcane, and the millets (*Panicum miliaceum* and *Setaria italica*) showed δC^{13} values of -12.2 to $-14.3‰$ relative to the PDB standard, enriched in C^{13} compared to wood. Corn is itself a tropical grass.

Tropical grasses have been of much interest in recent years inasmuch as photosynthetic studies have demonstrated that the path of photosynthetic carbon dioxide fixation in sugarcane and other tropical grasses from several tribes of Gramineae differs from the mechanism operative in other plants (Kortschak, Hartt, and Burr, 1965, and Hatch, Slack, and Johnson, 1967). Moreover the rate of photosynthesis of tropical grasses is higher than the rate for grasses of temperate origin (El-Sharkawy and Hesketh, 1965). Such a pronounced difference in metabolism apparently also results in a difference in carbon isotopic fractionation.

TABLE 1

Mass Spectrometric Analyses of Corn Samples

Sample	Locality	δ_C C^{13} relative to PDB standard
Archaeologic samples		
charred corn kernels	Aztalan site, Dane County, Wisconsin (Middle Mississippian)	—11.1‰
charred corn cob	Clement site, McCurtain County, Oklahoma (McCurtain focus, Fulton aspect)	—12.4‰
charred corn cob	Marr site, Bryan County, Oklahoma (Bryan focus)	—12.6‰
corn cob (uncharred)	Aravaipa Canyon, Pinal County, Arizona (Hohokam)	—12.4‰
Modern sample		
corn cob (uncharred)	Price County, Wisconsin	—13.2‰
	average	—12.3‰

TABLE 2

Mass Spectrometric Analyses of Grasses (Gramineae) for C^{13}/C^{12} Ratios

Tribe	Genus	Species	Common name	δ_C C^{13} relative to PDB
Panicoideae sub-group				
Andropogoneae	*Saccharum*		Sugarcane	—13.7‰
Andropogoneae	*Sorghum*		Sorghum	—12.2‰
Andropogoneae	*Sorghum*	*sudanense*	Sudan grass	—13.0‰
Maydeae	*Zea*	*mays*	Corn	—11.1 to —13.2‰
Paniceae	*Paspalum*	*notatum*	Bahia grass	—13.2‰
Paniceae	*Digitaria*	*sanguinalis*	Crabgrass	—12.7‰
Paniceae	*Setaria*	*italica*	Millet	—13.3‰
Paniceae	*Setaria*	*viridis*	Green foxtail	—13.3‰
Paniceae	*Panicum*	*miliaceum*	Millet	—14.3‰
Paniceae	*Panicum*	*capillare*	Tumble panic grass	—14.5‰
Festucoideae sub-group				
Festuca	*Dactylis*	*glomerata*	Orchard grass	—26.6‰
Avena	*Avena*		Oats	—27.0‰
Hordea	*Triticum*	*sativum*	Wheat	—26.9‰
Hordea	*Hordeum*		Barley	—27.8‰
Agrostelia	*Phleum*		Timothy	—28.2‰

The grasses which have been shown by Hatch *et al.* (1967) to follow the photosynthetic pathway similar to sugarcane are taxonomically related and belong to the same two sub-groups, either the Panicoideae or the Chloridoideae (Stebbins, 1956, Prat, 1960). Wheat, oats, timothy, and barley are classified as belonging to the Festucoideae sub-group and their photosynthesis has been found to follow the Calvin cycle and not the sugarcane cycle. Other grasses analyzed on the mass spectrometer which belonged to the Festucoideae sub-group showed δC^{13} values of -26 to $-28‰$, those of the Panicoideae sub-group showed δC^{13} values of -11.1 to $-14.5‰$.

Since cereals and grasses have been extensively used for radiocarbon dating purposes, it is obvious that the material must be accurately identified or the carbon isotopic composition determined. Variations in the C^{14}/C^{12} ratio are accepted as being twice the variations in the C^{13}/C^{12} ratios (Rafter, 1955) and, as a result, an enrichment of about 13‰ in the C^{13} of corn used as a sample for radiocarbon dating would result in a 26‰ enrichment in C^{14} relative to wood; this would result in a radiocarbon age 210 years younger than wood of the same actual age.

The carbon isotope ratios were measured with a precision of $\pm$ 0.1‰ in $\delta_C C^{13}$ on carbon dioxide produced by combustion of the samples in a Parr bomb. All samples were treated with hot dilute HCl to remove any occluded carbonates, washed with distilled water, and dried before combustion.

A Nuclide Corporation RMS6-60 isotope ratio mass spectrometer was employed in the comparison of the unknown CO_2 sample to a local tank standard. The resulting initial δ values were corrected for tailing of the m/e 44 peak, instrument background, and cross-contamination of samples through valve leakage. A shift of reference to the PDB standard was then made by comparing the local standard CO_2 with gas samples prepared by action of 85% and 100% phosphoric acid on a Pee Dee belemnite sample. The $\delta_C C^{13}$ values listed in Tables 1 and 2 were then calculated as described by Craig, assuming a value of 15‰ for δO^{18} for the combusted gas samples. Any error in these values due to lack of actual oxygen isotope ratio determinations, or to uncertainty in the instrument correction factors, can be expected to be negligible here.

In summary it should be noted that the variations in the C^{13}/C^{12} ratios in grasses depend upon the taxonomic relationships of the grasses and apparently not upon the soil or microclimate. Grasses from Tribes which are members of the Panicoideae sub-group may differ as much as $+220$ years and probably not less than $+160$ years in radiocarbon age from the average contemporary wood.

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