

Stable Isotope Ratios of Carbon in Phytoliths as a Quantitative Method of Monitoring Vegetation and Climate Change

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The ¹³C/¹²C ratios of occluded carbon within opal phytoliths from the northern Great Plains show potential as a basis for paleoclimatic reconstruction. A significant correlation exists between the carbon isotopic composition of a host plant and that of the organic matter in its phytoliths. The ¹³C/¹²C ratios for phytoliths from surface layers of soils along climatic gradients reflect the current proportions of C₃ and C₄ plants. Variations in the δ¹³C values of phytoliths with soil depth are caused by a variety of processes: burial of soil surface by dust, bioturbation, and possible illuviation by percolating water. Also, contributions of phytoliths by dust and roots have unknown isotopic effects. The δ¹³C values of phytoliths from soils increase with decreasing ¹⁴C age, suggesting that the proportion of C₄ plants in this region has increased during the Holocene. Phytoliths of apparent mid-Holocene age suggest exclusive dominance by C₄ plants which agrees with paleoclimatic interpretations of an arid middle Holocene climate. © 1991 University of Washington.

INTRODUCTION

Opal phytoliths are microscopic opaline particles formed within plant cell walls. Members of the *Gramineae* produce large amounts of phytoliths (Jones *et al.*, 1963), although phytoliths also occur in other plant families. Following the death and decomposition of a plant, phytoliths disperse and become a ubiquitous component of soils, comprising up to 1% of the total soil mass in grasslands (Jones and Beavers, 1964). Opal phytoliths are resistant to weathering and have been reported in the Pleistocene paleosols of Olduvai Gorge (Hay, 1976), Pliocene sediments in California (Nambudiri *et al.*, 1978), Miocene sediments in Kansas (Thomasson *et al.*, 1986), and the Oligocene Badlands of South Dakota (Retallack, 1983).

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Previous studies involving the use of opal phytoliths for paleoenvironmental reconstruction have focused mainly on their morphology (Twiss *et al.*, 1969; Twiss, 1987; Piperno, 1988). The relative amounts of opal phytoliths have been used successfully to differentiate grassland soils from those that support forests (Jones and Beavers, 1964) and to separate short grass from tall grass species (Twiss *et al.*, 1969). The usefulness of morphological studies of opal phytoliths for environmental reconstruction is predicated on the ability to identify phytoliths from ecologically diverse biota. Some complications arise due to the wide variation in phytolith morphology within a given plant, between parts of a given plant, and between members of plant groups, although progress is being made in minimizing those difficulties (Rovner, 1986).

There is a need for additional quantitative tools to reconstruct climate and vegetation in North American grasslands. In this region palynological information is scarce due to the absence of lakes and bogs (Ritchie, 1976; Webb *et al.*, 1983). In addi-

tion, pollen studies cannot distinguish ecologically diverse groups within the *Gramineae* (Ritchie, 1976), limiting their ability to detect climatically induced vegetation change in grassland environments.

Phytoliths have carbon concentrations of 1 to 5 wt% (Jones and Beavers, 1963; Jones and Milne, 1963). A portion of the total organic carbon contained within phytoliths is considered to be "occluded" since it is not susceptible to oxidation and is presumed to be physically protected. Previous work has shown the occluded carbon to be a suitable substrate for ^{14}C dating (Wilding, 1967). The purpose of this work is to explore the possibility of using the stable isotopic composition of carbon in phytoliths to reconstruct aspects of paleoenvironmental conditions.

The basis for this approach is related to the influence of climate on the distribution of C_3 and C_4 grasses. The relative proportions of C_3 and C_4 grasses growing at a site reflect climatic conditions, with higher minimum summer temperature and lower soil moisture favoring higher proportions of C_4 plants (Terri and Stowe, 1976; Ehleringer, 1978; Tieszen *et al.*, 1979). The $\delta^{13}\text{C}$ values (see Methods for definition) of C_3 and C_4 plants differ by substantial amounts, with the former being more ^{13}C -depleted than the latter (Bender, 1968; Smith and Epstein, 1971). The $\delta^{13}\text{C}$ value of carbon in the soil phytoliths thus should reflect environmental conditions if three conditions are met. First, the $\delta^{13}\text{C}$ value of the occluded carbon in a phytolith must be related to the $\delta^{13}\text{C}$ value of the host plant. Second, the $\delta^{13}\text{C}$ value of the carbon in soil phytoliths must not be susceptible to diagenetic alteration. Third, the ratio of C_3 to C_4 phytoliths deposited in a soil must be proportional to the ratio of C_3 to C_4 biomass growing at the site.

Laboratory and field studies were conducted to establish that the three conditions stated above are satisfied. Our results demonstrate the potential of this new method for paleoenvironmental reconstruction. We

then measured the variation in the carbon isotope composition of phytoliths with depth in soils from sites across a portion of the northern Great Plains. Based on ^{14}C dating of some of these phytoliths, we conclude that the younger phytoliths are derived from a predominantly C_4 flora whereas the older (early Holocene) phytoliths were derived from C_3 -based grasses.

SITE LOCATION AND DESCRIPTION

We studied six virgin prairie sites along two climatic gradients, one of decreasing precipitation (east to west) and the other of increasing temperature (north to south) (Fig. 1). Mean annual temperature ranges from 6.1° to 10.7°C in a north-to-south direction, while mean annual precipitation increases from 39.5 to 62.5 cm from west to east (Table 1). Approximately 75% of the annual precipitation occurs between April and September. Soils, situated on well-drained sites, are developed in late Wisconsin to Holocene-aged loess (Flint, 1955; Ruhe, 1984) and are classified as Mollisols characteristic of grasslands (Soil Survey Staff, 1987). The native rangeland vegetation along the temperature gradient (north-to-south direction) is mixed grass prairie, while along the precipitation gradient (west to east), three major grassland communities are differentiated: short, mixed, and tall grass prairies (Sims *et al.*, 1978).

METHODS

We collected soil and above-ground plant samples at each of the six study sites. The species composition and annual biomass of the native vegetation were estimated along two line transects and from quadrats (Phillips, 1959). The dominant C_3 and C_4 species were collected and returned to the laboratory for extraction of phytoliths. All plants were washed with dilute HCl, rinsed with water, and oven-dried prior to extraction. Phytoliths were extracted from the plants by wet oxidation procedures that utilize concentrated H_2SO_4 and 30% H_2O_2 (Geiss, 1978).

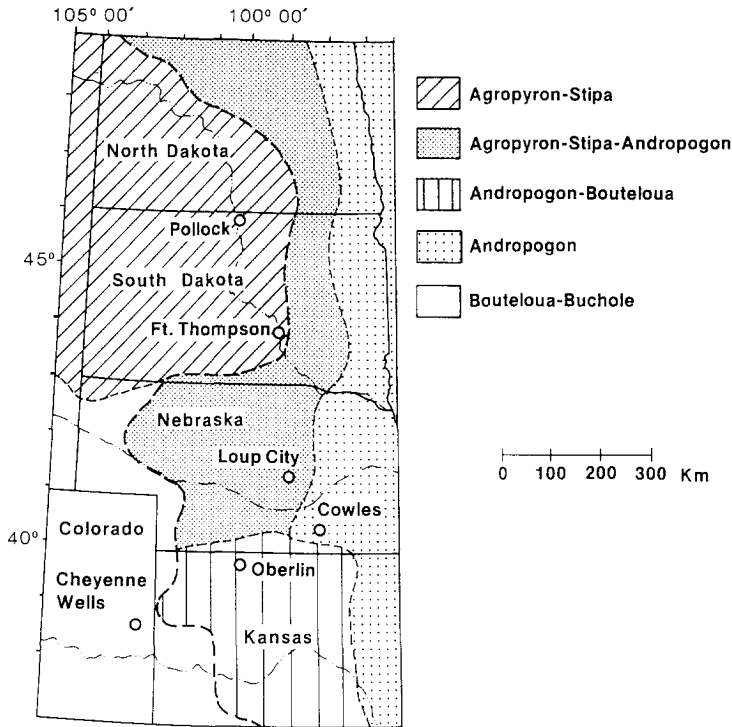


FIG. 1. Map showing locations and dominant grassland communities for each of the study sites.

Soils were sampled in 5-cm increments to the base of the A horizon or a depth of 30 cm, whichever was deeper. Phytoliths were extracted from the sand- and silt-size frac-

tions (2 to 200 μm) using standard particle-size sedimentation techniques (Jackson, 1969) and a zinc bromide heavy liquid separation procedure (Fredlund *et al.*, 1985).

TABLE 1. CLIMATE, VEGETATION, AND STANDING BIOMASS AT THE STUDY SITES

	Pollock, South Dakota	Ft. Thompson, South Dakota	Loup City, Nebraska	Cowles, Nebraska	Oberlin, Kansas	Cheyenne Wells, Colorado
	Dominant vegetation					
	Agsm Stco	Agsm Bogr	Ange Bogr	Ange Sonu Ange	Bogr Agsm	Buco Bogr
	C_3/C_4 of standing biomass					
1987	1.77	1.70	0.30	0.10	0.40	0.09
1988	0.32	0.96	0.10	0.19	0.10	0.20
	Standing biomass ($\text{kg} \cdot \text{ha}^{-1}$)					
1987	3364	4116	4120	2708	2640	936
1988	1877	2805	1511	2340	1260	280
MAT ($^{\circ}\text{C}$) ^a	6.1	7.8	10.7	11.7	11.5	11.4
MAP (cm) ^a	40.4	42.5	49.6	62.5	51.4	39.5

Note. Agsm = *Agropyron smithii* (C_3); Bogr = *Bouteloua gracilis* (C_4); Buco = *Buchole dactyloides* (C_4); Ange = *Andropogon gerardi* (C_4); Stco = *Stipa comata* (C_3); Sonu = *Sorghastum nutans* (C_4).

^a Based on 45-yr records from 1941 to 1986.

Upon recovery, all phytolith samples were washed with hot 6 N HCl, rinsed with water, and freeze-dried.

Prior to isotopic analysis both plant and soil phytolith samples were boiled in 18% H₂O₂ for a period of 6 hr, rinsed with water, freeze-dried, and pulverized. Plant and soil samples for which isotopic analysis of organic matter was to be done were treated with dilute HCl, rinsed with water, and oven-dried. Carbon concentrations and isotopic compositions were determined by combusting the samples at 875°C, purifying the resulting CO₂ cryogenically, and determining its quantity and isotopic composition manometrically and mass spectrometrically (Northfelt *et al.*, 1981). The carbon isotopic compositions are expressed in the δ notation where

$$\delta^{13}\text{C} = \left[\frac{(^{13}\text{C}/^{12}\text{C})_{\text{sample}}}{(^{13}\text{C}/^{12}\text{C})_{\text{standard}}} - 1 \right] \times 1000\text{‰}$$

The standard is Peedee belemnite (PDB) carbonate. The precisions of determination

of carbon concentrations and $\delta^{13}\text{C}$ values were ± 0.01 wt% and $\pm 0.1\text{‰}$.

RESULTS AND DISCUSSION

The dominant photosynthetic pathway (C₃ or C₄), biomass production, and species composition of the native grassland vegetation varied as a function of climate (Table 1). The opal phytolith production, as reflected in the amounts recovered from the soil surface at each site, should be closely related to the amounts of precipitation, temperature, and subsequent transpirational uptake of H₄SiO₄ (Yeck and Gray, 1972; Jones and Beavers, 1964). Quantities of opal recovered from the two Nebraska sites (with high transpiration rates) were greatest, while the Colorado site (with low rainfall) and the Pollack, South Dakota site (with cool temperatures and low transpiration) contained the lowest quantities of opal phytoliths (Figs. 2a, 2b).

The $\delta^{13}\text{C}$ values for occluded carbon in phytoliths were highly correlated with, but

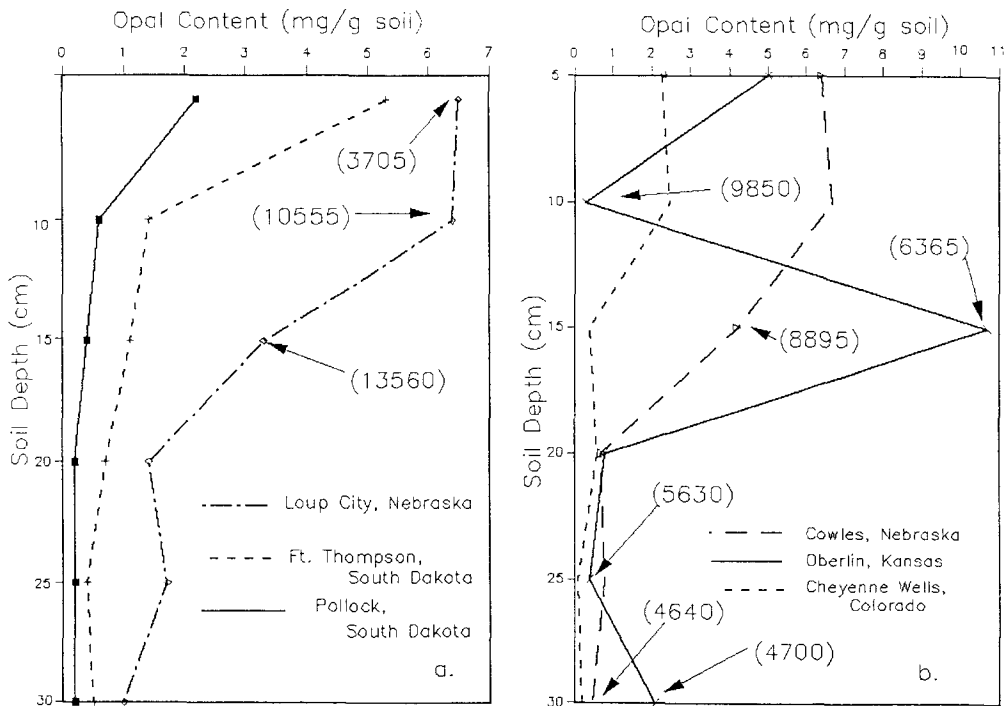


FIG. 2. Opal phytolith concentration vs soil depth at each study site for (a) the temperature and (b) the precipitation gradients. The apparent AMS ¹⁴C of dated samples are given in parentheses.

were significantly depleted in, ^{13}C relative to those for the host plant tissue (Fig. 3, Table 2). The differences between phytolith and plant tissue $\delta^{13}\text{C}$ values may reflect higher concentrations of such ^{13}C -depleted components as lipids (Parker, 1964) or lignin (Benner *et al.*, 1987) in the phytolith organic matter relative to plant leaf tissues. If this explanation is correct, the greater difference between plant tissue and phytoliths for C_4 plants ($-7.8 \pm 1.5\%$) relative to that for C_3 plants ($-3.5 \pm 0.6\%$) may be caused by higher concentrations of lipids and lignins in the phytoliths of the former relative to those in the latter. The chemical nature of the occluded phytolith carbon is not well known (Wilding *et al.*, 1967). Diffused reflectance Fourier transform infrared spectroscopy of phytoliths indicated the presence of aromatic compounds as indicated by the 1500-, 1630-, and 1876- cm^{-1} absorption bands, which would be consistent with the presence of lignin (Kinney and Doucette, 1958; Hergert, 1960; Bolker and Terashima, 1966). ^{13}C NMR experiments yielded inconclusive results due to the low concentration of carbon in the phytoliths. Further chemical studies may allow our hypothesis to be tested. The strong correla-

TABLE 2. THE $\delta^{13}\text{C}$ VALUES OF PLANT TISSUES AND PHYTOLITH CARBON AT EACH STUDY SITE

	Photo-synthetic pathway	$\delta^{13}\text{C}$ value	
		Plant	Phytolith
Pollock, South Dakota			
<i>Agropyron smithii</i>	C_3	-26.3	-28.9
<i>Bouteloua gracilis</i>	C_4	-13.9	-23.0
Ft. Thompson, South Dakota			
<i>Agropyron smithii</i>	C_3	-26.8	-30.0
<i>Panicum virgatum</i>	C_4	-16.8	-23.7
Loup City, Nebraska			
<i>Agropyron smithii</i>	C_3	-25.3	-29.0
<i>Andropogon gerardi</i>	C_4	-12.1	-20.9
<i>Bouteloua gracilis</i>	C_4	-14.0	-22.0
<i>Andropogon scoparius</i>	C_4	-16.0	-23.0
Cowles, Nebraska			
<i>Andropogon gerardi</i>	C_4	-12.1	-22.3
<i>Bouteloua gracilis</i>	C_4	-14.9	-22.1
<i>Andropogon scoparius</i>	C_4	-15.9	-21.5
Oberlin, Kansas			
<i>Bouteloua gracilis</i>	C_4	-13.1	-21.8
<i>Buchole dactyloides</i>	C_4	-12.0	-21.3
<i>Sporobollus cryptandrus</i>	C_4	-12.0	-27.7
<i>Stipa comata</i>	C_3	-24.2	-27.7
Cheyenne Wells, Colorado			
<i>Buchole dactyloides</i>	C_4	-14.9	-21.9
<i>Bouteloua gracilis</i>	C_4	-13.9	-19.9
<i>Buchole dactyloides</i>	C_4	-14.4	-20.8
<i>Stipa comata</i>	C_4	-24.3	-26.6

tion between the $\delta^{13}\text{C}$ value of the host plant and that of its phytoliths, however, makes isotopic analysis of soil phytolith carbon a potentially useful paleoenvironmental tool.

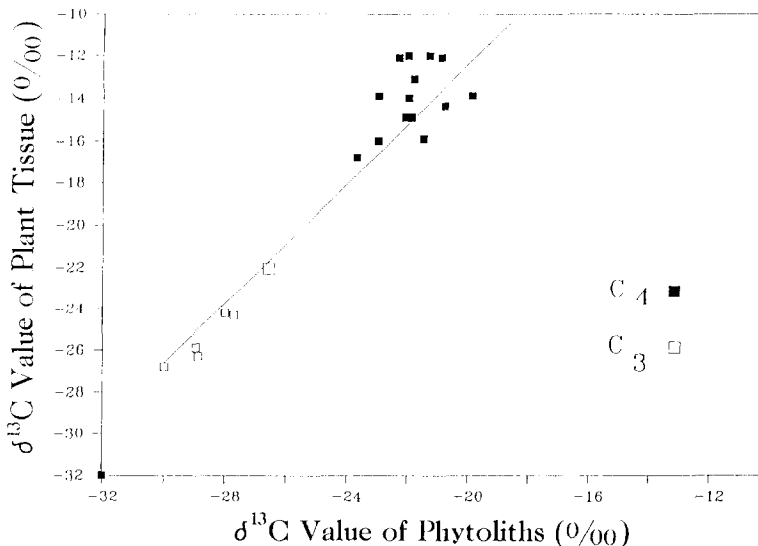


FIG. 3. Correlation between the $\delta^{13}\text{C}$ values of plants and opal phytoliths ($r^2 = 0.93$; $y = 1.6x + 21.0\%$).

The resistance of the occluded carbon to diagenesis was tested by subjecting opals to a series of vigorous oxidations with hydrogen peroxide (Wilding, 1967). We found the mean carbon content of the phytoliths extracted from plants prior to this oxidation to be 0.8 ± 0.2 wt% ($n = 24$). Boiling the phytoliths in 18% H_2O_2 for 6 hr reduced the organic carbon content to 0.2 ± 0.2 wt% ($n = 20$), with further boiling in H_2O_2 having no effect. This indicates that surficial organic carbon is oxidized by the H_2O_2 , leaving behind occluded carbon that is protected from oxidation by the nonporous, glass-like opal microstructure. Phytoliths extracted from soils were subjected to the same H_2O_2 treatment. Initial carbon contents of 1.2 ± 0.4 wt% ($n = 12$) were reduced to 0.4 ± 0.3 wt% ($n = 31$) by the hydrogen peroxide oxidation. Any post-mortem contaminants adhering to the phytoliths would be oxidized in this treatment, leaving behind only occluded carbon within the phytolith that should retain its *in vivo* isotopic composition. The similarity of the organic carbon concentrations extracted from the plants and soils supports this contention.

$\delta^{13}C$ values of phytoliths extracted from the top 5 cm of soils vary as a function of climate and dominant vegetation (Table 3). The northernmost sites, which had a greater abundance of C_3 plants, had $\delta^{13}C$ values in the 0- to 5-cm depth lower than those of sites with predominantly C_4 plants.

Based on the relationship between $\delta^{13}C$ values of the opal phytoliths and their host plants (Fig. 3), we calculated the percentage C_3 vegetation indicated by the $\delta^{13}C$ val-

ues of opal phytoliths from the 0- to 5-cm depth in the soils. These isotopic mass balance calculations are based on mean $\delta^{13}C$ values of -20.8 ± 0.9 and -28.4 ± 1.1 ‰ for carbon in C_4 and C_3 phytoliths, respectively. For example, if soil phytoliths had a $\delta^{13}C$ value of -23.5 ‰, this would indicate a mixture of 36% C_3 and 64% C_4 plants. Similar mass balance calculations were done from the $\delta^{13}C$ values of the organic matter in the A1 horizon at each study site. For these calculations we assumed mean $\delta^{13}C$ values of -25.4 and -14.0 ‰ for organic matter from C_3 and C_4 plants, and a 2‰ shift toward more positive values for plant organic matter $\delta^{13}C$ values during decomposition (e.g., O'Brien and Stout, 1978; Nadelhoffer and Fry, 1988). If the actual isotopic shift in organic matter during decomposition is less than 2‰, then the percentage of C_3 -derived organic matter would be less than we calculated.

The calculated percentage of C_3 plants based on the carbon isotopic composition of the phytoliths in the surface soil layer agreed with the values observed for the present biomass at four sites and with the percentage calculated from the $\delta^{13}C$ value for the soil organic matter at five sites (Table 4). The largest differences between the calculated and the observed biomass values occur at the sites in Colorado and Cowles, Nebraska. The Colorado site was grazed in recent years (C. Lovell, personal communication, 1990), which may have selectively reduced the proportion of C_3 plants and may be partially responsible for the discrepancy between observed and measured C_3 abundances. However, the soil organic

TABLE 3. $\delta^{13}C$ VALUES OF OPAL PHYTOLITHS EXTRACTED FROM THE SOILS AT EACH STUDY SITE

Soil depth (cm)	Pollock, South Dakota		Ft. Thompson, South Dakota		Loup City, Nebraska		Cowles, Nebraska		Oberlin, Kansas		Cheyenne Wells, Colorado	
	Horizon	$\delta^{13}C$	Horizon	$\delta^{13}C$	Horizon	$\delta^{13}C$	Horizon	$\delta^{13}C$	Horizon	$\delta^{13}C$	Horizon	$\delta^{13}C$
0-5	A1	-25.4	A1	-25.3	A1	-22.7	A	-23.4	A1	-22.4	A1	-24.8
5-10	A1	-25.4	A1	-25.9	A1	-22.6	A	-23.5	A2	-24.0	A2	-24.0
10-15	A1	-26.0	A1	-23.2	A2	-23.2	A	-23.3	A2	-21.5	A2	-23.9
15-20	A2	-26.4	A1	-26.2	A2	-25.4	A	-25.9	A2	-25.1	Bt	-26.2
20-25	A2	-26.2	BAk	-25.5	Bt1	-20.0	BAt	-22.7	Bt1	-21.4	Bt	-20.9
25-30	A2	-23.9	BAk	-24.5	Bt1	-20.9	BAt	-21.6	Bt2	-21.1	Bt	-19.9

TABLE 4. PERCENTAGES OF C₃ PLANTS AT STUDY SITES BASED ON STANDING BIOMASS MEASUREMENTS, ON $\delta^{13}\text{C}$ VALUES OF SOIL PHYTOLITHS AT 0- TO 5-CM DEPTH, AND ON $\delta^{13}\text{C}$ VALUES OF SOIL ORGANIC MATTER

	% C ₃ Plants					
	Pollock, South Dakota	Ft. Thompson, South Dakota	Loup City, Nebraska	Cowles, Nebraska	Oberlin, Kansas	Cheyenne Wells, Colorado
	From standing biomass					
1987	64 ± 3	62 ± 13	21 ± 4	12 ± 2	17 ± 5	14 ± 3
1988	24 ± 3	48 ± 4	7 ± 1	16 ± 1	11 ± 4	12 ± 5
	From soil organic matter $\delta^{13}\text{C}$ values (A1 Horizon)					
	61	48	29	24	20	22
	From soil phytolith $\delta^{13}\text{C}$ values (0- to 5-cm depth)					
	60 ± 13	58 ± 13	24 ± 11	34 ± 12	21 ± 11	42 ± 12

matter $\delta^{13}\text{C}$ values also suggest a lower C₃ plant percentage than that predicted by the phytolith isotope ratio. As the 1987 and 1988 standing biomass data indicate, the relative proportion of C₃ and C₄ plants varies from year to year. Since the phytoliths in the upper 5 cm of the soil reflect a relatively long-term accumulation, complete agreement between the estimates of C₃ plant abundance from 1987 and 1988 biomass measurements and soil phytolith $\delta^{13}\text{C}$ values is not necessarily expected. However, the close agreement for most of the sites, and the fact that C₃ abundances indicated by soil phytolith isotope ratios follow expectations based on the known distribution of C₃ and C₄ plants, indicates that surficial soil phytolith $\delta^{13}\text{C}$ values are relatively good indicators of recent vegetation.

SIGNIFICANCE OF VARIATIONS IN THE $\delta^{13}\text{C}$ VALUES OF CARBON IN PHYTOLITHS IN THE SOIL PROFILES

The $\delta^{13}\text{C}$ values of phytolith carbon vary with soil depth (Table 3), indicating that differences in the relative proportions of C₃ and C₄ phytoliths occur with depth. What processes might lead to such a heterogeneous distribution of phytoliths?

One possible scenario is that continuous dust deposition (and a slow, continuous burial of the soil surface), in conjunction with downward migration of phytoliths by bioturbation and leaching, has led to the de-

velopment of a soil profile that records climatic and vegetational changes stratigraphically. In this case, the oldest phytoliths are found at depth and the age of the phytoliths should decrease nearer the present-day soil surface. In support of this hypothesis, we estimate that the upper 30 cm of the soils may have been deposited during the past 5000 to 10,000 yr based on present-day dust deposition rates (Smith *et al.*, 1970). This is also supported by Ruhe (1984), who showed that the mineralogy of the upper 50 cm of these soils is more like that of the present dust than that of the underlying loess.

A second explanation is that the variation in phytoliths with depth is the result of a complex set of processes that mix phytoliths from different plants, and from different times, in an unpredictable depth/time pattern. Some of the processes that may contribute to this include bioturbation (which may transport material upward as well as downward), the addition of phytoliths from plant roots (which would add young phytoliths to older phytoliths at depth), and illuviation of phytoliths (or fragments) by downward-moving water.

Nine phytolith samples extracted from soil horizons in the Nebraska and Kansas sites were ¹⁴C-dated by accelerator mass spectrometry (AMS) (Linick *et al.*, 1986). The results (Table 5) show that all the phytolith samples are Holocene to latest Pleis-

TABLE 5. $\delta^{13}\text{C}$ VALUES AND APPARENT AMS ^{14}C AGES OF SELECTED PHYTOLITH SAMPLES

Site location	Depth (cm)	$\delta^{13}\text{C}$ value	Age (yr B.P.)
Oberlin, Kansas	5-10	-24.1	9850 \pm 75
	10-15	-21.5	6365 \pm 70
	20-25	-21.4	5630 \pm 60
	25-30	-21.2	4700 \pm 50
Cowles, Nebraska	10-15	-23.3	8895 \pm 70
	25-30	-21.6	4640 \pm 55
Loup City, Nebraska	0-5	-22.6	3705 \pm 50
	10-15	-23.6	10,555 \pm 65
	15-20	-25.4	13,560 \pm 80

tocene in age, in agreement with the presumed age of the loess deposits themselves (Ruhe, 1984). The apparent ^{14}C ages of the phytoliths from the Loup City soil increase in age with increasing soil depth, supporting the first explanation discussed above. However, the ages of the samples from soils at the Cowles and Oberlin sites decrease in age with increasing depth. The processes responsible for these differing results are examined below.

Numerous studies have shown that opal phytolith concentrations are greatest at the soil surface and decrease in a regular manner with increasing depth (Jones and Beavers, 1964). This is true for both the Loup City and the Cowles soils (Fig. 2). However, the Oberlin soil has an extremely irregular distribution of opals with depth, suggesting that extensive bioturbation by gophers and/or prairie dogs has occurred. No visible indication of such activity was present in the profile chosen for sampling, although prominent krotovinas were present on other walls of the soil pit that was excavated. Even though the mixing had been masked by organic matter additions, apparently the effects of past bioturbation are still evident in the phytolith distribution. Therefore, it is reasonable to expect that the age of phytoliths should not increase with depth in a regular manner downward through this soil profile.

A second important observation is that in the Cowles soil the apparent ^{14}C age of phytoliths for the 25- to 30-cm depth is nearly

half that of phytoliths in the 10- to 15-cm depth, despite the regular distribution of opal phytoliths that exists (Fig. 2). At the depth where the "age reversal" occurs, the total phytolith concentration is quite low. Thus, it is possible that root additions of phytoliths from a C_4 plant (note the less negative ^{13}C value of this sample) may have added a significant proportion of phytoliths near the lower portions of the A horizons. The importance of root contributions to total soil phytoliths is not known with certainty. Geiss (1978) showed that roots contain only 25% of the opal phytoliths that aboveground components do in three important grass species. However, depending on the rates of root turnover, the total contribution of phytoliths by roots could be nearly as large as the aboveground contribution (Geiss, 1978). In contrast, calculations by others (Yeck and Gray, 1972) indicate that the total amount of phytoliths in a soil profile can be nearly accounted for by the present rate of aboveground production and the age of the soil, suggesting that roots will make only a substantial contribution in the lower portions of the profile where inputs from aboveground phytoliths were low. It is also possible that the relatively young phytoliths or phytolith fragments have been preferentially translocated downward by percolating soil waters. Demonstration of the relative importance of the processes described above would require further study.

Except for the youngest sample, the $\delta^{13}\text{C}$ values of the phytoliths for all samples that were dated increase with decreasing age (Fig. 4). Unlike the ^{14}C age of soil organic matter, which gives a mean residence time (due to constant losses of organic matter) (Stevenson, 1982), the ^{14}C age of the phytolith samples gives a mean age of all the phytoliths that are present. Thus, all that can be said with certainty regarding the data in Figure 4 is that as the proportion of young phytoliths in a sample increases, the $\delta^{13}\text{C}$ values increase, indicating that the more recently formed phytoliths are derived from a C_4 -rich biomass. A more spec-

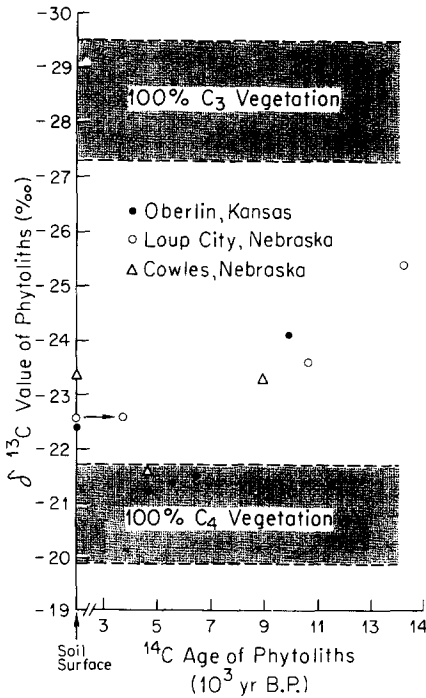


FIG. 4. The relationship between the $\delta^{13}\text{C}$ values and apparent ^{14}C age of the phytoliths. The 100% C_3 and C_4 regions were calculated using the mean values \pm one standard deviation of the phytoliths extracted from C_3 and C_4 plants.

ulative interpretation of the data is that the apparent ^{14}C age of the phytoliths crudely represents the absolute age of the sample. If this were the case, the trend for $\delta^{13}\text{C}$ vs time would be roughly what would be ex-

pected for the Great Plains from the late Pleistocene to the present: high C_3 biomass in the latest Pleistocene or early Holocene, highest C_4 biomass during the mid-Holocene altithermal, and greater C_3 biomass today than in the mid-Holocene (Grüger, 1987; Van Zandt, 1979; Hall, 1982; Ritchie *et al.*, 1983). Unfortunately, this interpretation cannot be proven (or disproven) with the data at hand. We emphasize that the alternative interpretation (that the ^{14}C age of any sample is a mixture of phytoliths from a large time span) is equally plausible, and that possibly no absolute chronological information can be gathered from Figure 4.

There are two pieces of evidence that partially support an absolute age interpretation of the phytolith ^{14}C data. First, the $\delta^{13}\text{C}$ value of disseminated organic carbon in the unaltered loess at the base of the three soils is extremely depleted in ^{13}C relative to the present-day organic matter in the A horizons (Fig. 5). This ^{13}C -depleted organic matter was undoubtedly incorporated into the loess at the time of its deposition since (i) these samples are well below the present rooting depth, (ii) these samples lie below the zone of obvious chemical weathering and average depth of water penetration, and (iii) the organic matter cannot have been transported by leaching since

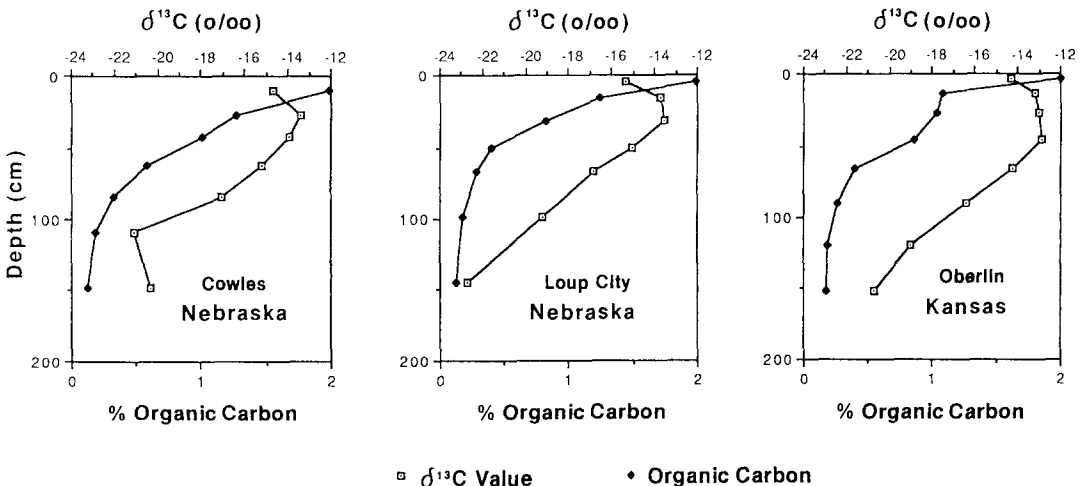


FIG. 5. The content and $\delta^{13}\text{C}$ values of organic matter in soils in which opal phytoliths were ^{14}C dated (\blacklozenge , organic carbon concentration, \square , $\delta^{13}\text{C}$ value).

fulvic acid, the most mobile portion of the soil organic matter, is enriched in ^{13}C relative to the bulk organic matter (Nissenbaum and Schallinger, 1974). Assuming that the organic matter at the base of the profile has undergone a 2‰ shift during decomposition (O'Brien and Stout, 1978; Nadelhoffer and Fry, 1988), mass balance calculations suggest it was derived from a biomass consisting of 76 to 94% C_3 plants. In comparison, the $\delta^{13}\text{C}$ value for the 11,660-yr-old phytolith sample indicates it is composed of approximately 63% C_3 phytoliths, in reasonable agreement with the estimate for organic matter, which must be, at the youngest, early Holocene. The second line of evidence supporting an absolute age interpretation of the phytolith ^{14}C contents is that samples between 4000 and 7000 yr old contain more C_4 phytoliths than older or younger samples (Fig. 4). Simple mixing could not have produced these samples, which, based on their $\delta^{13}\text{C}$ values, may be derived totally from C_4 plants. However, as discussed above, possibly these samples reflect only the C_4 portion of the biomass that was present at that time due to extensive root contributions or selective movement.

CONCLUSIONS

The $\delta^{13}\text{C}$ values of occluded carbon in opal phytoliths provide a potentially useful paleoenvironmental tool. Although the occluded phytolith carbon is depleted in ^{13}C relative to the whole plant tissues, there is a strong correlation between plant and phytolith $\delta^{13}\text{C}$ values. In addition, the $\delta^{13}\text{C}$ values of carbon in phytoliths from the present soil surface correspond reasonably well to the present vegetation, indicating the potential of isotopic analysis of phytoliths to record information on vegetation assemblages.

The availability of AMS makes the dating of small phytolith samples possible and a chronological interpretation of phytolith samples from soils feasible. The results of our study involving ^{14}C dating and stable isotope analysis suggest that latest Pleisto-

cene or early Holocene flora was dominated by C_3 grasses, which decreased in abundance in later Holocene vegetation. The youngest average age of soil phytoliths appears to be at the soil surface, but general statements about age–soil depth relationships are impossible to make at this time. The age–depth relationship at any site appears to be the result of several geologic and biological processes whose relative importance probably varies from site to site.

Stable isotope analysis of occluded phytolith carbon is an important tool that can be added to a growing body of research involving phytoliths (Piperno, 1988); however, more work is needed to understand fully the processes that distribute phytoliths in soils. Stable isotope analysis, combined with morphological study, should be a fruitful means of studying vegetation in paleosols spanning large ranges in geologic time because the carbon occluded in phytoliths is likely to be highly resistant to diagenetic breakdown and contamination.

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