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THE CHEMICAL VARIABILITY OF CARBONIZED ORGANIC MATTER THROUGH TIME

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ABSTRACT

The interdependent dynamics of climate, biota, relief, parent material and time affect the evolution of both soils and archaeological remains within the soil. Carbonized organic matter, charcoal, is one class of archaeological material subject to these environmental factors. Although charcoal is generally presumed to be immune to environmental influences, chemical analyses of feature soils containing charcoal from archaeological sites throughout New England demonstrate its susceptibility to the effects of environmental factors. Calculation of a formula of the interdependent dynamics of these environmental factors provides some understanding of the specific influences of each factor. This formula, when expressed in terms of the factor time, provides an independent, inexpensive and accurate means to determine the age of archaeological charcoal. The low cost and ease of this procedure is well-suited to environmental, geological and archaeological disciplines. Since this is a chemical procedure, relatively young charcoal can be dated without the problems found in radiocarbon dating of young charcoal.

INTRODUCTION

The interdependent dynamics of climate, biota, relief, parent material and time are generally recognized as the prime causes for the development of soils (Jenny 1941). As soil constitutes the contextual matrix of most archaeological deposits, these five factors are likely to have an influence on certain classes of archaeological deposits. One such class, carbonized organic matter or charcoal, is affected by these five soil formation factors in ways that have implications for archaeological research. Organic matter, whether used for food, clothing, structures, tools or fuel, constitutes the largest class of cultural remains. However, this particular class of artifacts is extremely susceptible to biochemical alterations in its form, (i.e., decay), and dispersement of its parts due to natural recycling and leaching of elements. The net result is that little surviving evidence of this class of cultural material is found in an archaeological context (Schiffer 1987).

One form of organic matter which does survive in archaeological context is carbonized organic matter resulting from human activities (i.e., cooking hearths) or natural events (e.g., environmental fires)(Schiffer 1987). Carbonized organic matter, often referred to as charcoal, consists mainly of elemental carbon and inorganic compounds, and is generally thought to be immune to biochemical decay and natural recycling (e.g., Dowman 1970).

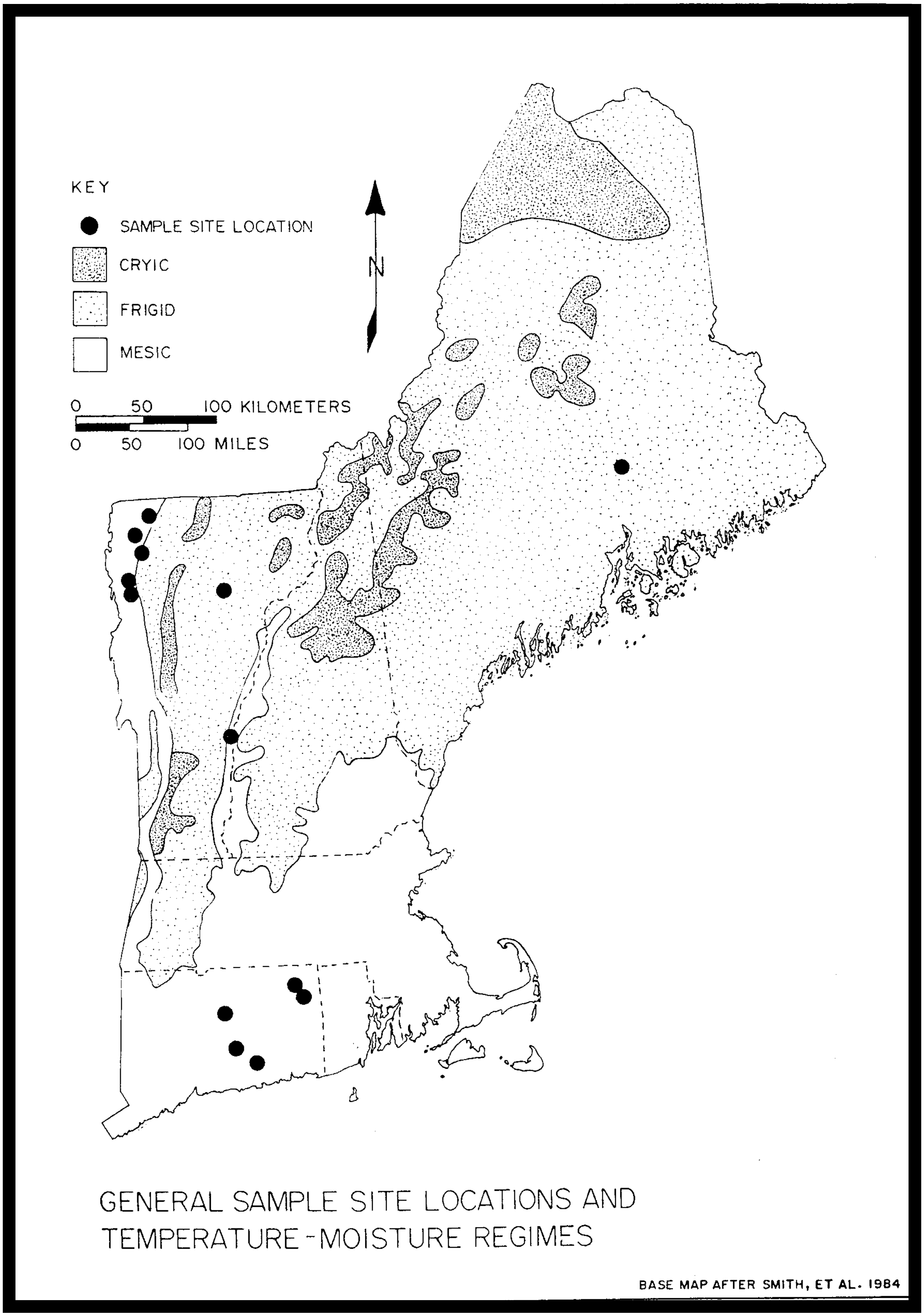
Archaeologists focus much of their field research on the recovery of charcoal-containing features, specifically hearths, storage pits, and burned secular and sacred structures. When excavated by the archaeologist, these features generally are recognized as spatially limited disturbances in the natural soil structure. The soils inside the feature include the mineral soils normal to the area mixed with charcoal and often other cultural artifacts. Due to the enhanced resistance to decay afforded by carbonization, these features are likely to contain important information on foodways, technological innovations/adaptations, and perhaps other types of information not normally found elsewhere on the site. Furthermore, these charcoal-containing features provide a means to obtain statistically probable dates from radiometric analysis of the charcoal. The literature, ranging from site reports to journal articles, abounds with discussions on the number and type, or the absence, of these charcoal-containing features in specific sites. However, despite the dependence on charcoal for dating archaeological sites, research results are not available concerning the potential alteration of charcoal through time within the soil context.

If charcoal changes through time, the changes must be understood before productive research designs can be constructed. Charcoal physically exists for long periods of time, making it available for radiometric dating of archaeological sites tens of thousands of years old. Nevertheless, it is essential to recognize that its chemical and structural composition may be altered by the same factors affecting the soils which surround it.

METHODS

Fifty-eight soil samples from features containing charcoal from archaeological sites in Connecticut, Maine and Vermont were collected for analysis (Figure 1). Contextual site information was recorded for the samples, including depth below surface, reactivity (pH), texture, associated soil series, slope, aspect and temperature-moisture

Figure 1. Sample site locations and temperature-moisture regimes in the study area.



regime. All soil samples were taken from below the organically enriched pedogenic A and E-horizons and/or below the plow zone. The age of the charcoal was provided through radiocarbon dating; or when radiocarbon was unavailable, through temporally diagnostic artifacts found in, or associated with, the sampled feature.

Twenty-seven archaeological sites dating from the Early Archaic period through the recent European American period are represented in the sample; nine are located in Connecticut, four in Maine, and fourteen in Vermont. These sites include stratified floodplain sites, open-air encampments in plowed fields and in unplowed forests, and rockshelter sites.

Most of the samples used in this study were obtained as a result of state or federally mandated archaeological environmental review studies. Although many of these studies were conducted at the Phase I (site identification) level only, some Phase II (site evaluation) and Phase III (data recovery) studies are also represented. Cultural and environmental information for most of the sites used in this study are available only in technical reports which have limited circulation (reports on file with each state's Historic Preservation office). However, more widely available journal articles and published reports are available for some of the sites in each state (Frink 1984; McBride 1978; Ott and Frink 1988, 1986; Petersen 1991; Petersen et al. 1985).

Carbon is a natural component of the soil normally composing one to five percent of the upper soil horizon (the A, E, and plow zone horizons). Below the organically enriched A-horizon, natural carbon is much less in evidence, generally composing less than 0.05% of the soil. This carbon consists of plant and animal residues, microorganisms, stable humus, and highly carbonized compounds of elemental carbon, such as charcoal. Of these, the elemental forms of carbon are the most resistant to biochemical alteration. As the elemental carbon component does not significantly contribute to the agronomic value of soils, little research has been conducted involving the agents causing the biochemical alteration of charcoal in the soil context.

The chemical analyses used in this study focused on the presumed stability of charcoal over time. The samples were analyzed for total carbon using the Ball Loss on Ignition procedure (Ball 1964). This procedure involves heating the dried soil sample in a muffle furnace at temperatures of 375o C for 16 hours. The loss in weight of the sample is due to the total oxidation (to CO2) of the carbon.

The amount of readily oxidizable carbon by wet combustion was determined using the Walkley-Black procedure (Walkley 1935; Walkley and Black 1934). The wet combustion procedure was originally designed to measure the more biologically active forms of carbon such as raw organic material and soil humus, while excluding most of the inorganic and elemental forms of carbon. Charcoal, which agronomically is considered to be a form of elemental carbon, would be expected to contain very little measurable readily oxidizable carbon. Thus, the readily oxidizable carbon measured by the Walkley-Black procedure is expected to be significantly less than the total carbon determined by the Loss on Ignition procedure due to the predominance of carbonizedorganic matter (charcoal) in the sample. Generally, the results obtained from these procedures are converted to percent organic matter for agronomic purposes. As the focus of this study is charcoal, the data have not been converted to organic matter. These two procedures were chosen due to the relatively abundant research and literature available on these procedures, and because of the low cost and simplicity of the procedures.

The chemical stability of charcoal was determined through the comparison of the ratio of the readily oxidizable carbon to total carbon in each sample, (the Oxidizable Carbon Ratio, or "OCR"). If charcoal is environmentally stable, the OCR of each sample should be similar or be randomly distributed independent of the five soil formation factors of climate (i.e., temperature and moisture regimes), biota (i.e., pH and depth below surface), relief (i.e., slope and aspect), parent material (i.e., texture and soil series), and time (i.e., radiocarbon date or temporally diagnostic artifact).

The data in the categories of Climatic Regime and Textures were given an arbitrary scale for statistical analyses. Climatic regimes are theoretical constructs derived from the combined influence of precipitation and temperature on soil development. The mesic and frigid climatic regimes were assigned values of 10 for mesic in Connecticut, 9 for mesic in Vermont, 8 for the area at the interface between mesic and frigid, and 7 for frigid in Vermont and Maine. Soil Taxonomy (Soil Survey Staff 1975) defines the mesic regime as having a mean annual soil temperature from 8o to <15o C (47o to 59o F). The frigid regime is defined as having a mean annual soil temperature ranging from 0o to <8o C (32o to 47o F). Precipitation for the New England area varies between 70 and 105 cm (33 and 43 inches) per year.

Soil Texture affects soil development by regulating the diffusion of moisture and atmospheric gases. Soil textural classes were assigned values of 2 for silt loams, 3 for fine sandy loams, 4 for loamy sands, and 5 for sands. The archaeological sites from which these samples were taken are located on flat to very gently sloped landscapes. Thus, the factor of relief is assumed to be a constant for all samples used in this study.

Of the 58 samples evaluated, 48 have also yielded radiocarbon dates. This subset of 48 samples will be used for the primary analysis. The remaining 10 samples will be discussed later. Of the 48 samples, 10 are from Connecticut, 19 are from Maine, and 19 are from Vermont.

Various agronomic studies have been conducted comparing the results for total organic matter (including all forms of organic carbon) for the Walkley-Black and Ball Loss on Ignition procedures on soil samples obtained from the organically enriched A, E and Plow zone horizons. For surface organically enriched horizons(A, E, and plow zone) the Total Organic Carbon varies from 30.3% to 62.5% (by weight) of the organic matter in the soil, depending on the type of vegetative matter and its degree of decomposition (Broadbent 1953). For Amadon's samples, Total Organic Carbon constituted 51% of the organic matter (Amadon 1979). Amadon (1979) found a strong correlation (r=.96) between readily oxidizable carbon and total carbon content with the Walkley-Black procedure, recovering an average 79% of the Total Organic Carbon in the sample. Similar percentage were found by other studies: 76% (Walkley 1947), 75% (Bonemisza, et al. 1979).

RESULTS

A similarly strong correlation (r=.94) between the results of the Walkley-Black and Loss on Ignition procedures is evident in the data used in this study (Table 1). A strong correlation may indicate that the two procedures are interchangeable, or that "normal" topsoil organic matter consists of a relatively constant composition of plant and animal residues, microorganisms, stable humus, and highly carbonized compounds of elemental carbon, such as charcoal. However, unlike the studies cited above that focused on the relationship between the results from these procedures, this study examines the relative environmental stability of carbonized organic matter through time.

A high degree of variability is evident in the OCR ratio in the archaeological samples in this study, ranging between 2.53 and 7.12, with a mean of 3.91, and a standard deviation of 1.09. This high degree of variability suggests that charcoal may not be as immune to biochemical alteration within the archaeological context as previously thought.

In order to determine the influence of the factor of soil formation on this variability, the OCR is compared to each of the environmental attributes listed above. Relatively low positive or negative correlations were found between the OCR and

TIME (r = +.35), DEPTH (r = +.31), % CARBON (r = +.21), CLIMATIC REGIME (r = -.37) and TEXTURE (r = -.24). Virtually no correlation is indicated for OCR and pH (r = +.06). Thus, no single factor can clearly account for much of the variability in the OCR values. The interdependent dynamics of these variables may strongly affect the chemical change of carbon in the soil.

A multiple linear regression calculation for the OCR and these six variables provides a moderate correlation (r = .63). If the variability in the OCR is the result of soil formation processes, this interdependent dynamic needs to be examined. Before studying these relationships, a brief discussion of the six variables and their expected effect on the OCR is necessary.

EXPECTED ENVIRONMENTAL ATTRIBUTE EFFECTS

Rainfall and temperature, the primary components of climatic regimes, affect soil development in several ways. Jenny (1941) found that with increased rainfall soil pH decreases, indicating that the extent of leaching and organic decomposition decreases. Depth to leached carbonates in the soil increases. Nitrogen content, indicating degree of organic decomposition in the soil, and clay content, indicating leaching and mineral decomposition in the soil, increases. For every 10o centigrade rise in temperature, the speed of chemical reactions increases by a factor of 2 to 3 (Van't Hoff 1884). If the variability in the OCR is the result of biochemical action, samples obtained from archaeological sites in the mesic climatic regime will have a lower OCR than samples from the frigid climatic regime because chemical reactions will be slightly faster in the warmer, mesic regime.

Soil depth and texture affect the rate of oxygen diffusion, and thus the growth and depth of root development (Stolzy et al. 1961). With an increase in depth, the oxygen concentration decreases, and concurrently root growth decreases. Coarse-textured soils show a higher rate of oxygen diffusion, with a corresponding increase in the rate and depth of root growth. Root growth and biochemical change are both oxygen dependent. If the variability in the OCR is the result of biochemical action, OCR readings will be lower in samples from near the surface, and higher as the depth increases. Also, the degree of variability with depth will be less for coarse-textured soils and greater for fine-textured soils.

As presented earlier, most soil carbon research has focused on the more environmentally dynamic organic carbons found in the soil, such as plant and animal residues, microorganisms and stable humus. The carbonized or burned forms of carbon,

Table 1. Data used to derive the equations presented in this paper, accompanied by archaeological site provenience. Column headings are aligned with the left margin of the columns that they describe. For example, **OCR RATIO, LOSS ON IGNITION,** and **WALKELY-BLACK** results are the second, third and fourth columns from the right, respectively.

CASE#	STATE	REGIME	SITE#	FEATURE#	DEPTH	TEXTURE	pH	14C DATE	+/-	14C LAB#	WALKLEY-BLACK	LOSS ON IGNITION	OCR RATIO	NOTES
01	CT	MESIC	105-3		15 cm	ROCK	5.1	270	60	β-7811	19.61	58.97	3.01	PAST
02	CT	MESIC	6-WD-63-1	1	100 cm	LS	5.6	4830	120	I-13028	2.16	6.93	3.21	ACT
03	CT	MESIC	6-HT-89	1	125 cm	FSL	5.0	3690	80	QC-305	1.58	3.99	2.53	PAST
04	CT	MESIC	105-34	1	15 cm	ROCK	5.0	3610	70	β-7808	15.48	51.18	3.31	PAST
05	CT	MESIC	6-2D-19-6	5	45 cm	FSL	4.60	3950	60		0.72	2.05	2.85	PAST
06	CT	MESIC	6-WD-19-6	2	40 cm	FSL	5.3	3130	90		0.98	3.09	3.15	PAST
07	CT	MESIC	6-WD-19-6	3	25 cm	FSL	5.4	2060	90		1.93	7.69	3.98	PAST
08	CT	MESIC	105-33	1	15 cm	ROCK	4.0	2700	60	β-7810	8.62	33.33	3.87	PAST
09	CT	MESIC	22-8		27 cm	FSL	5.0	1550	50	β-7816	9.59	46.92	4.89	PAST
10	CT	MESIC	6-?-163-2		10 cm	LS	5.0	270	110	β-7814	7.15	39.19	5.48	PAST
11	CT	MESIC	54-23	1	60 cm	LS	6.0	1300	EST		0.83	1.82	2.19	PAST
12	ME	FRIGID	69-14	4	35 cm	FSL	5.4	3210	100	β-18,222	0.39	1.69	4.33	UMF
13	ME	FRIGID	90-3	1	35 cm	SIL	5.5	3740	100	β-19970	0.64	2.46	3.84	UMF
14	ME	FRIGID	90-2C	20	110 cm	SIL	5.7	6195	55	PITT-695	0.84	3.78	4.73	UMF
15	ME	FRIGID	90-2C	19	50 cm	SIL	5.4	2005	50	PITT-694	1.27	4.73	3.72	UMF
16	ME	FRIGID	90-2C	18	80 cm	SIL	5.6	5235	35	PITT-693	0.50	3.56	7.12	UMF
17	ME	FRIGID	90-2C	28	160 cm	SIL	5.8	7940	190	β-20363	0.37	2.39	6.46	UMF
18	ME	FRIGID	90-2C	17	75 cm	SIL	5.5	4055	40	PITT-692	0.85	3.96	4.66	UMF
19	ME	FRIGID	90-2C	15	30 cm	SIL	4.5	1875	35	PITT-691	2.26	7.73	3.42	UMF
20	ME	FRIGID	90-2C	14	15 cm	SIL	4.5	1020	60	PITT-690	1.20	4.64	3.87	UMF
21	ME	FRIGID	90-2D	7	90 cm	FSL	6.6	3650	110	β-20,719	0.68	3.82	5.62	UMF
22	ME	FRIGID	90-2D	18	175 cm	FSL	5.9	8250	320	β-18,235	1.38	4.89	3.54	UMF
23	ME	FRIGID	90-2D	20	176 cm	FSL	6.1	6320	110	β-18,234	1.71	6.04	3.53	UMF
24	ME	FRIGID	92-2D	21	135 cm	FSL	6.1	7200	140	β-18,236	0.44	3.04	6.91	UMF
25	ME	FRIGID	69-14	6	40 cm	FSL	5.7	2910	70	β-18,224	0.72	2.76	3.83	UMF
26	ME	FRIGID	69-14	11	40 cm	FSL	5.7	3190	70	β-18,225	0.68	2.79	4.10	UMF
27	ME	FRIGID	69-14	11	40 cm	FSL	5.7	3020	90	β-18,227	0.83	3.47	4.18	UMF
28	ME	FRIGID	69-14	11a	35 cm	FSL	5.7	2900	120	β-18,228	0.64	3.18	4.97	UMF
29	ME	FRIGID	69-14	11	35 cm	FSL	5.7	2510	60	β-18,226	0.69	2.80	4.06	UMF
30	ME	FRIGID	69-14	18	50 cm	FSL	5.5	3090	140	β-18,229	0.57	2.22	3.89	UMF
31	VT	MES-FRIGID	VT-FR-219	6	15 cm	FSL	4.0	810	80	β-40659	1.52	5.13	3.38	ACT
32	VT	MES-FRIGID	VT-FR-219	2	30 cm	FSL	4.0	1900	60	β-40656	1.65	5.37	3.25	ACT
33	VT	MES-FRIGID	VT-FR-219	3	15 cm	FSL	4.0	1350	90	β-40657	1.20	4.54	3.78	ACT
34	VT	MES-FRIGID	VT-FR-219	4	15 cm	FSL	4.0	800	100	β-40658	1.27	4.39	3.46	ACT
35	VT	MES-FRIGID	VT-FR-219	7	15 cm	FSL	4.0	660	80	β-40660	1.51	4.98	3.30	ACT
36	VT	MES-FRIGID	VT-FR-219	8	12 cm	FSL	4.0	650	100	β-40661	1.39	4.74	3.41	ACT
37	VT	MESIC	VT-CH-430	1	30 cm	FSL	6.4	2180	90	β-38440	0.70	2.37	3.39	ACT
38	VT	MESIC	VT-CH-430	2	20 cm	FSL	5.8	1500	90	β-38441	0.82	2.63	3.21	ACT
39	VT	MESIC	VT-WN-61	3	61 cm	FSL	6.0	1530	120	β-45389	0.95	2.51	2.64	ACT
40	VT	MES-FRIGID	VT-FR-161	1	45 cm	SIL	5.9	3170	80	β-12929	1.35	3.82	2.83	CAP
41	VT	MES-FRIGID	VT-FR-140	4	55 cm	FSL		7970	270	β-8418	1.05	3.59	3.42	CAP
42	VT	MES-FRIGID	VT-FR-161	2	45 cm	SIL	5.9	2520	90	β-11718	1.63	5.63	3.45	CAP
43	VT	MES-FRIGID	VT-FR-161	3	45 cm	SIL	4.7	4290	60	β-11717	1.16	2.94	2.53	CAP
44	VT	MES-FRIGID	VT-LA-1	2	20 cm	LS	6.5	1500	EST		0.27	1.29	4.78	ACT
45	VT	MESIC	VT-CH-315	2	20 cm	LS	5.2	1170	90	β-29100	0.60	2.05	3.42	ACT
46	VT	MESIC	VT-CH-238	3	35 cm	SIL	6.5	3250	EST		0.94	2.67	2.84	CAP
47	VT	MESIC	VT-CH-5	4	10 cm	LS	7.2	250	50	β-9880	1.15	4.25	3.70	UVM
48	VT	MESIC	VT-CH-5	6	15 cm	LS	7.2	260	90	β-9882	2.60	7.20	2.77	UVM
49	VT	MESIC	VT-CH-5	7	35 cm	LS	6.8	1250	270	β-9883	1.28	3.95	3.09	UVM
50	VT	MESIC	VT-CH-234	2	45 cm	FSL	5.5	2500	EST		1.63	4.42	2.71	CAP
51	VT	MESIC	VT-CH-201	2	20 cm	LS	5.0	1200	EST		0.76	2.51	3.30	CAP
52	VT	MESIC	VT-CH-201	4	20 cm	LS	4.0	1200	EST		0.63	2.11	3.35	CAP
53	VT	MESIC	VT-CH-294	1	45 cm	FSL	5.5	3250	EST		0.67	1.86	2.78	ACT
54	VT	MESIC	VT-CH-219	2	30 cm	FSL	4.0	1900	60	β-40656	13.72	84.43	6.15	ACT
55	VT	FRIGID	VT-WA-22	1	5 cm	S	7.6	98	1		2.29	6.87	3.00	ACT
56	VT	MESIC	BEACH		.5 cm	S	8.3	1	EST		3.32	29.53	8.89	ACT
57	VT	MESIC	BRUSH1		.5 cm	S	9.9	2	EST		1.21	5.06	4.18	ACT
58	VT	MES-FRIGID	BRUSH2		.5 cm	S	8.8	1	EST		0.84	4.36	5.19	ACT

such as charcoal, are relatively resistant to biochemical alteration. Therefore, they are not considered to significantly contribute to the agronomic value of soils. For this reason, little research has been conducted involving the agents causing this biochemical alteration of charcoal. However, it may be surmised that microbial agents are involved, utilizing, although not dependent upon, the carbon for metabolic processes. The concentration of carbon may have only a limited effect on microbial populations. With this assumption, those samples having a higher percentage of carbon are expected to have higher OCR ratios.

The factor of time affects the rate and the duration of biochemical processes. Some variability in the OCR is expected to be the result of the age of the sample, with older samples show ing a lower OCR ratio. It is also expected that the rate of change in the OCR will decrease as the age of the sample increases. Soil pH affects both chemical and biological processes. It is expected that lower OCR ratios will be found in soils having higher pH values.

A MATHEMATICAL MODEL FOR OCR VARIATION

In combination, these interdependent variables influence the different OCR ratios. However, the relationship between each individual variable and the OCR ratio can not be expressed in linear "cause and effect" terms as demonstrated by the correlation statistics presented above. The influence of the interdependent variables on the OCR ratio must be expressed as a system where each variable's influence is balanced against the others'. As a balanced system, we can assume that it can be expressed by a mathematical formula, which will describe this system in a statistically normal manner.

This influence may be expressed by any number of mathematical formulas relating these variables to the OCR ratio. The sample used in this study only approximates the entire population. Therefore, while any number of mathematical expressions of these variables could be used to describe the entire population, certain mathematical expressions will describe the sample better than others. To determine which mathematical expression best describes the sample used in this study, the various possible formulas were solved for a constant (f). The formula having a constant which best describes the sample as a normal distribution was found to be:

$$f = \frac{(\text{OCR x REGIME x DEPTH})}{(\text{TEXTURE x \%CARBON x TIME x pH})} \text{ x } 1000 = 8.78936$$

Individual samples with an “f “ value significantly different from the mean were outliers which must be explained. Twelve of these samples were obtained from floodplain terraces, where deposition has been incremental over time. Because datable samples are present throughout the profile, the rate of deposition can be estimated to be roughly linear through time. Thus, the effect of depth on the OCR measurement for these samples is expected to be approximately half of the depth below surface, because the “average” depth at which they have been buried is only half the total depth. Two samples were obtained from former floodplain terraces where erosion has occurred. Unlike the previous cases, where incremental deposition could be documented, the rate and time of erosion are unknown. Four other samples were obtained from rock shelter sites, where overhanging rock faces have limited the effects of rainfall and solar radiation (Regime), and where post-occupational rock falls from the overhang have covered the feature, exaggerating the effect of depth. Recalculating the correlation between the OCR and the six variables without these definable outliers results in stronger correlation (r = .74).

As discussed above, the relative effect of the carbon concentration and pH on the OCR variability may not be linear. A stronger correlation (r = .84) is obtained when the square root of %carbon and pH are used. The final formulation is:

$$f = \frac{(\mathrm{OCR} \times \mathrm{REGIME} \times \mathrm{DEPTH})}{(\mathrm{TEXTURE} \times \sqrt{\%\mathrm{CARBON}} \times \sqrt{\mathrm{pH}} \times \mathrm{TIME})} \times 1000$$

From this formula, the “f “ value for the samples minus the defined outliers is 34.0538. The population distribution demonstratesa peaked normal curve (kurtosis = 4.69, skewness = 0.56) In the discussion of definable outliers presented above, it was suggested that the effective depth of 12 samples buried in the floodplain soils was roughly one half of the measured depth at the time of excavation. To test this hypothesis, the OCR formulation can be solved for depth:

$$\mathrm{OCR}_{\mathrm{DEPTH}} = \frac{(\mathrm{TEXTURE} \times \sqrt{\%\mathrm{CARBON}} \times \sqrt{\mathrm{pH}} \times \mathrm{TIME} \times f)}{(\mathrm{OCR} \times \mathrm{REGIME} \times 1000)}$$

A translation from the OCRDEPTH to the measured depth is found by generating a regression line for these two variables (r = .92).

Figure 2 shows the comparison between the calculated OCRDEPTH and the hypothesized effective depth (1/2 the measured depth below surface). With the exception of Samples 22 and 23, a strong correspondence is indicated between the hypothesized effective depth and the calculated OCRDEPTH. The calculated OCRDEPTH for Samples 22 and 23 clearly do not correspond to the hypothesized effective depth. The soil descriptions for these two samples, having the greatest depth and located in floodplain deposits adjacent to an active river, suggest that these samples may have been affected by multiple episodes of oxidation and reduction due to seasonal high water tables. (The chromic acid used in the Walkley-Black wet oxidation procedure is subject to interference by oxidizable or reducible soil constituents such as Cl-, Fe2+, and MnO2.) These comparisons between the hypothesized effective depth and the calculated OCRDEPTH suggest that with careful documentation of the soil strata of flood-deposited soils, the OCRDEPTH may approximate the effective depth of buried deposits under most well-drained to moderately well-drained conditions.

Discussion

Carbonized organic matter, charcoal, is not immune to environmental decay. The factors affecting this environmental decay and soil development are the same. Although the design of this study did not enable identification of the specific agents

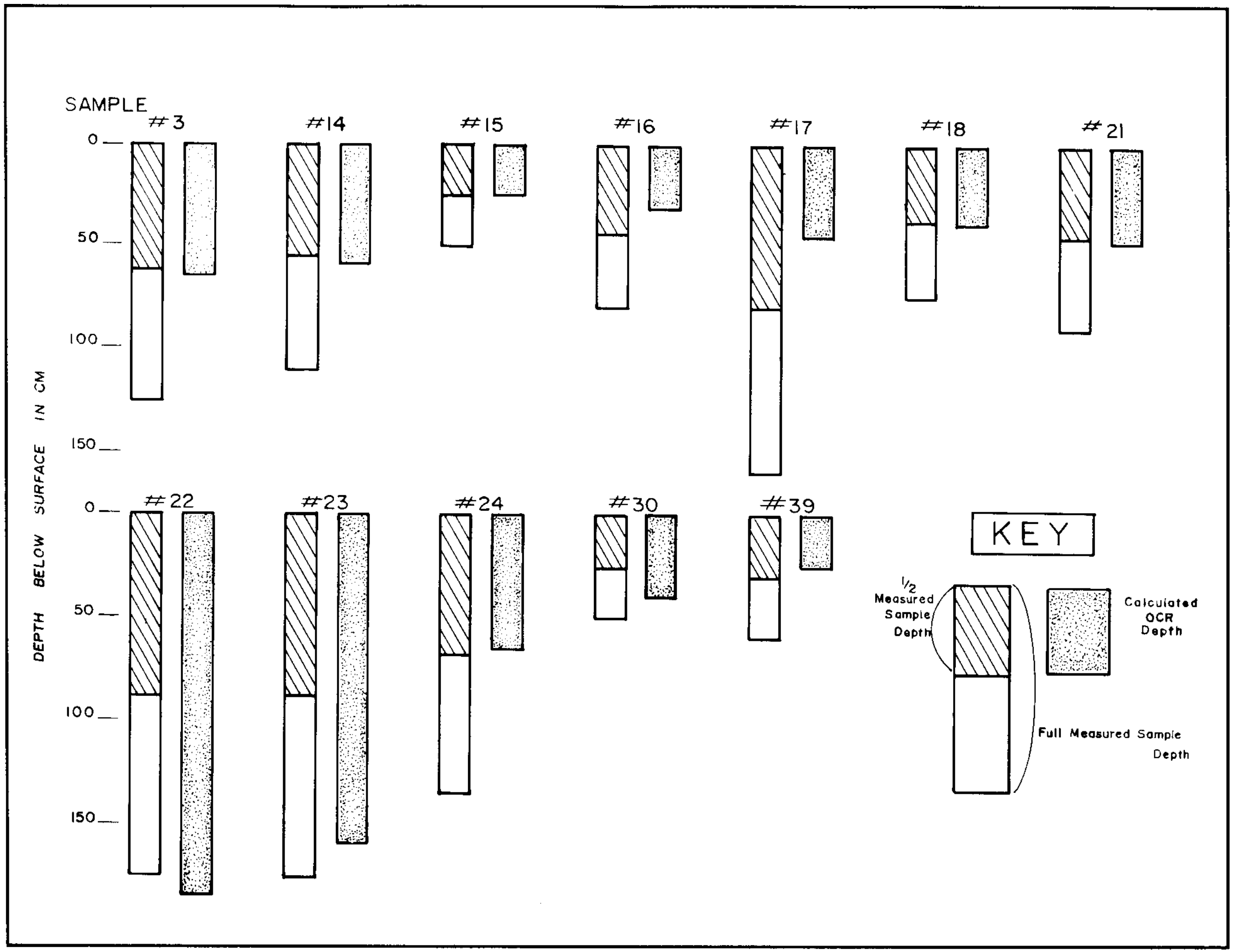


Figure 2. A graphic comparison between expected effective depth of burial in alluvial sediments and calculated OCR_{DEPTH}.

causing the change in the charcoal which is indicated by the variation in OCR, microorganisms and/or chemical reactions in the soil dependent on oxygen, moisture and temperature are likely involved in this process. A hypothetical model of the process involves the contamination, or alteration, of the carbon bonds (C=C) in the charcoal. At time-zero, the charcoal consists of a loose matrix of C=C chains in the pattern of the original cellular structure. Although agronomically considered to be a form of elemental carbon, charcoal is not crystalline, and is vulnerable to isomorphic substitution and breakage of the C=C chains. Through time, as a result of biochemical processes, the charcoal contains proportionally fewer C=C chains resistant to the Walkley-Black wet oxidation procedure, and a greater number of C=X (X=other) molecules which are readily oxidizable by this procedure.

The implications of the findings in this study go beyond establishing the susceptibility of charcoal to environmental degradation. The formulation presented above, explaining the dynamic relationship of the variables, can be solved for Time:

$$\mathrm{OCR_{TIME}} = \frac{(\mathrm{OCR\ x\ REGIME\ x\ DEPTH})}{(\mathrm{TE}\underline{\mathrm{XTURE\ x}\ \downarrow}\ \%\mathrm{C}\underline{\mathrm{AR}}\mathrm{BON\ x}\ \downarrow \mathrm{pH\ x\ f})}\ \mathrm{x}\ 1000$$

A translation between OCRTIME and radiocarbon date is obtained through the generation of the regression line for these two variables (Figure 3).

Using this formulation, it is possible to calculate the age of a given sample based on the OCR within the specific environmental context of the sample. In addition to the original 48 samples analyzed in this study, 10 samples dated only by temporally diagnostic artifacts were analyzed and the OCRTIME calculated. Figure 4 displays the relationship between the OCRTIME and the temporal range of the diagnostic artifacts. For Samples 11, 44, 46, and 50-53, the calculated OCRTIME dates fall within the time ranges suggested by the temporally diagnostic artifacts.

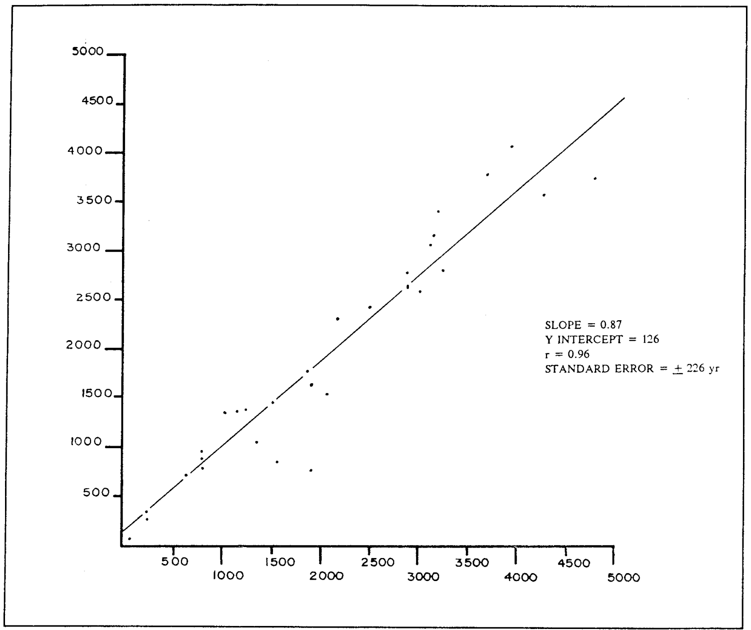


Figure 3. A regression line and data points comparing calculated $\mathrm{OCR_{TIME}}$ and C-14 radiometric date.

For the more recent samples (56-58), the correspondence is also excellent, considering the change in scale and the level of accuracy indicated by the standard error of the estimate of +226 years for the OCRTIME calculations.

This OCR formulation may be applied in a variety of ways. It can serve as a preliminary dating tool to select samples for the more costly radiometric dating procedures. These chemical procedures may be especially useful for detecting carbon samples younger than the effective minimum age of radiocarbon dating, especially so because they are of low cost. Moreover, isotopic contamination of "old" carbon released by industrial burning of fossil fuels, or of "young" post-1950 "bomb" carbon should not effect these chemical (non-isotope-related) measurements. The OCR formula may also provide an environmentally based correlate for measuring change through time in classes of archaeological data other than organic matter, or may be used both as a model and as a correlate for other signatures of pedological process.

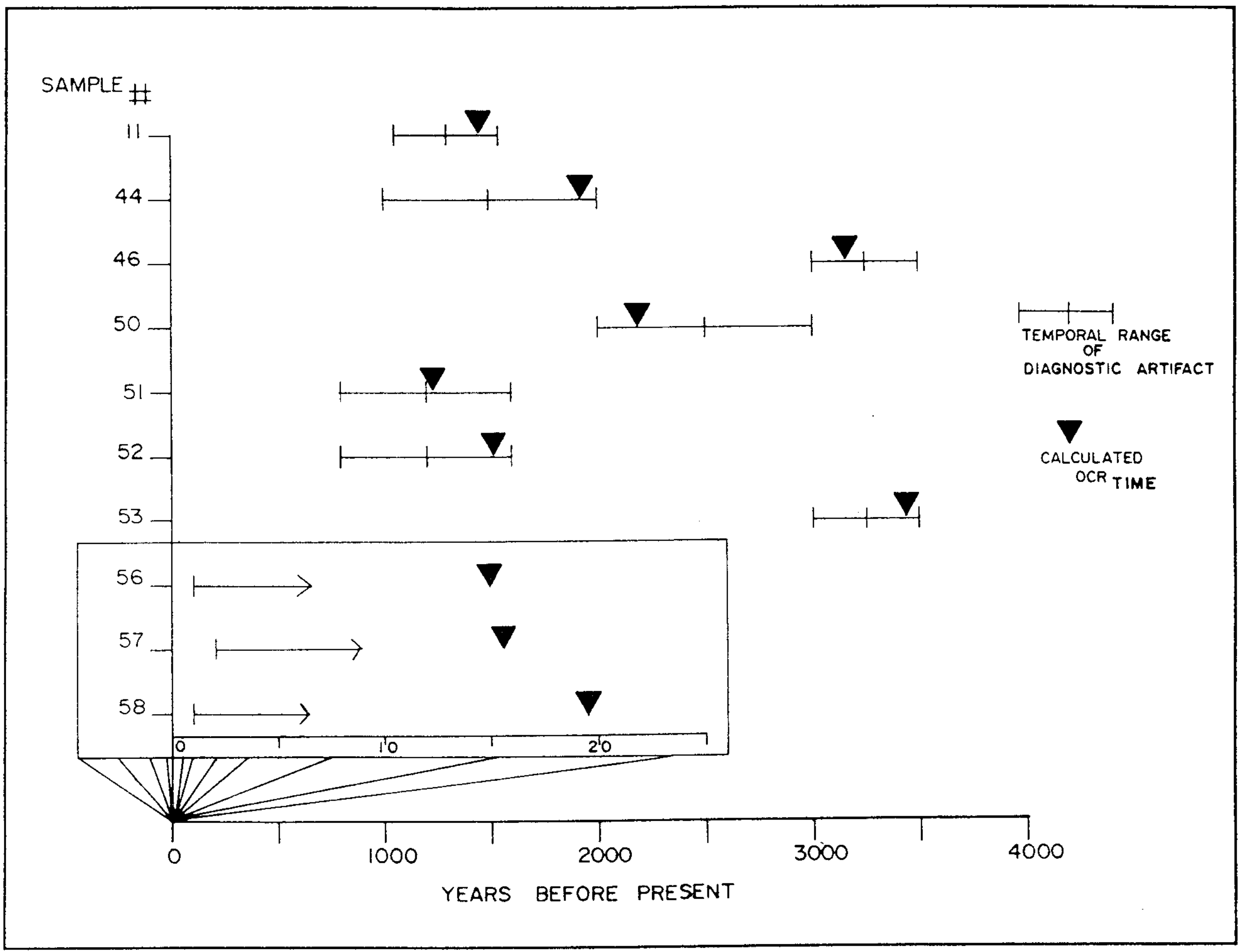


Figure 4. A graphic comparison between expected artifact age, based upon diagnostic artifacts associated with samples, and OCR$_{\text{TIME}}$

CONCLUSION

The formulas presented here are a first approximation of the process of change in the nature of charcoal through time. Precision in the formulas is limited by the arbitrary values given to soil textures and climatic regimes. As texture affects the rate of oxygen diffusion, the values given for texture should reflect actual diffusion rates. Climatic regimes are theoretical constructs derived from the combined influence of precipitation and temperature. Values derived directly from these two variables, including the seasonability of these two variables, should reflect their influence on biochemical processes in the soil.

With improved accuracy in the data, stronger correlations between each environmental factor and the calculated OCRTIME will be possible. As the formulas are refined, the margins of error for the calculated OCRTIME will become smaller, improving the utility of this procedure for the environmental, geological and archaeological disciplines.

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