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Application of the Oxidizable Carbon Ratio (OCR) Dating Procedure and its Implications for Pedogenic Research

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Abstract

The Oxidizable Carbon Ratio (OCR), expressed as the ratio of total C by loss-on-ignition to readily oxidizable C by wet oxidation, challenges the presumed biological stability of carbonized organic matter. Previous studies demonstrate that charcoal is biologically recycled at a slow, but measurable rate, and that the rate of biochemical degradation of the carbonized organic matter varies within the specific physical and environmental contexts of the sample. The OCR-dating procedure determines an age for the C sample by use of a systems formula designed to account for the biological influences of O2, moisture, temperature, C concentration and the media's (soil) reactivity. These variables are measured by soil texture and depth below the soil surface, the site-specific mean annual temperature and rainfall, percent of total C, and the soil pH. Residual influences on this system are included through a statistically derived constant. Using data from locations in North America and East Africa, a strong correlation [r = 0.98, standard error (SE) = 0.03] is demonstrated between the age estimates obtained by the OCR-dating procedure and 14C radiocarbon age estimates. Outliers define how river inundation and poor sample preparations adversely affect the results. This procedure is expanded to measuring the OCR of relatively stable residual organic matter, and to date the age of buried soil horizons. The OCR-dating procedure accounts for the interdependent dynamics of climate, biota, parent material, and time, providing an empirical test of Jenny's model for pedogenesis.

Recently published research data challengs the presumed biological stability of carbonized organic matter, or charcoal (Frink, 1994, 1992). These articles conclude that charcoal undergoes changes through time that can be detected by standard chemical soil analyses. Soil samples containing charcoal were obtained from archaeological contexts of known age throughout the New England states. The samples were analyzed for total C using the Ball Loss on Ignition procedure (Ball, 1964), and for readily oxidizable C using the Walkley-Black wet combustion procedure (Walkley, 1935; Walkley & Black, 1934). The results of these two chemical analyses demonstrate a decreasing linear relationship to time when expressed as a ratio of total C to readily oxidizable C. This ratio is called the OCR. The rate of biochemical degradation of the charcoal varies within the specific physical and environmental contexts of the sample. To determine an age for the C sample, a systems formula was designed to account for the biological influences of O2, moisture, temperature, C concentration and the media's (soil) reactivity. These variables are measured by soil texture and depth below the soil surface, the site specific mean annual temperature and rainfall, percentage of total C, and the soil pH. Residual influences on this system are included through a statistically derived constant (Frink, 1994).

Past studies have compared the results for total organic matter of the Walkley and Black and Ball Loss on Ignition procedures on soil samples obtained from the organically enriched A, E, and plow zone horizons (Amadon, 1979; Bonemisza et al., 1979; Walkley, 1947). The Walkley and Black procedure, however, measures only the more readily oxidizable C compounds in the soil and thus provides an incomplete measure of organic C. For surface organically enriched horizons (A, E, and plow zone), the total organic C recovered by the Walkley and Black procedure varies from 30.3 to 62.5% (w/w) of the organic matter in the soil, depending on the type of vegetative matter and its degree of decomposition (Broadbent, 1953). For carbonized organic matter, the recovery rate was found to be <36% (Bremner & Jenkinson, 1960). Due to the high variability in recovered organic C, the Walkley and Black procedure is considered to give only approximate or semiquantitative estimates of organic C in the soil (Nelson & Sommers, 1982).

Data from 14C radiocarbon analyses and historic documentation on the age of samples from archaeological sites throughout New England demonstrate a strong direct correlation between the age of the C and the amount of C recovered by the Walkley and Black procedure (Frink, 1992, 1994). The environmental factors that directly affect the relative oxidizability of the carbonized organic matter are rainfall, temperature, soil reactivity (pH), texture and depth of sample below surface (O2 permeability), and the total available C.

Rainfall and temperature affect soil development. Soil pH decreases with increased rainfall. Lower soil pH directly affects the extent of leaching and rate of organic decomposition (Jenny, 1941). For every 10o C rise in temperature, the rate of chemical reactions increases by a factor of 2 to 3 (Van't Hoff, 1884).

Soil depth and texture affect the rate of O2 diffusion, and thus the growth and depth of root development (Stolzy et al., 1961). As depth increases, O2 and root growth decreases. Coarse-textured soils have a higher rate of O2 diffusion, with a corresponding increase in the rate and depth of root growth. Carbonized or burned forms of C are relatively resistant to biochemical alteration, and are not believed to significantly contribute to the agronomic value of soils. For this reason, the microbial agents causing the biochemical alteration of charcoal have not been extensively researched. The factor of time affects the rate and the duration of biochemical processes. Soil pH affects both chemical and biological processes in the soil (Jenny, 1941).

Other factors, as yet unidentified, affecting the oxidizability of the carbonized organic matter are subsumed within a calculated constant. The relationship between variables in a system may be expressed by a number of mathematical equations; however, certain equations will describe the sample population better than others. The best equation will describe the sample population as a normal distribution curve with the highest Kurtosis. The various possible equations were solved for a population of 58 samples,and the following equation and constant were statistically determined to be the best description of this system.

$$\frac{\text{OCR} \times \text{Depth} \times \text{Mean temperature} \times \text{Mean rainfall}}{\text{Mean texture} \times \sqrt[2]{(\text{pH})} \times \sqrt[2]{(\%\ \text{C})} \times \text{Time}} = f = 14.4888.$$

This equation may be reworked to solve for the variable Time, expressed as OCRDATE, which may then be used in calculating an age estimate for other carbonized organic matter samples.

$$\text{OCR}_{\text{DATE}} = \frac{\text{OCR} \times \text{Depth} \times \text{Mean temperature} \times \text{Mean rainfall}}{\text{Mean texture} \times \sqrt[2]{(\text{pH})} \times \sqrt[2]{(\%\ \text{C})} \times 14.4888}$$

A high degree of correlation ($r = 0.98$; $SE = 0.03$) exists between known dates from empirical data obtained from recently documented events or 14C estimates (Fig. 6-1), and the age estimates obtained from the OCR procedure (Frink, 1994). The age estimates obtained through the OCR-dating procedure can be used to corroborate the date estimates obtained through radiocarbonanalyses, or, as is the case for charcoal <300-yr-old, provide age estimates where radiocarbon data provides little interpretable information.

While the OCR procedure provides good age estimates for many archaeological samples, it cannot be applied to all situations. Specific environmental conditions must be met before meaningful age estimates are possible. The change in the oxidizable C ratio through time and the formulation of the OCRDATE equation, were derived from samples obtained from moderately to well drained aerobic soils. Results from the analyses conducted on samples obtained from poorly drained anaerobic soils yielded spurious data, suggesting that OCRDATE equation pertains to an O2 dependent system. Soil samples affected by long-term saturation (reducing conditions) returned age estimates much older than expected. This is probably due to interference by reduced Cl, Fe and Mn ions (Walkley, 1947) and depressed rates of aerobic microbial action on the samples. Samples obtained from sealed or protected contexts, such as under stone paving, returned uninterpretable results due to the uncalculated effect of exposure to rainfall, temperature, and soil O2 (Frink, 1992).

The potential use of the OCR procedure goes beyond dating archaeological samples. The fundamental assumption of Jenny's (1941) model of soil genesis is that soils are the result of the interdependent dynamics of climate, biota, relief, parent material, and time. The formula used to calculate the OCRDATE estimate describes a similar balanced system. The relationship between each of the individual variables cannot be expressed in linear cause and effect terms. Rather, the effect of changes in one variable will be distributed throughout the equation by changes in one or more variables. By describing a balanced system, this formula provides an empirical expression of Jenny's (1941) model. The OCR formula reflects the variables of climate (mean rainfall and temperature), biota (depth below surface, percentage of C, and pH), parent material (soil texture and pH), and time. Although the archaeological samples used in these two studies were obtained from topographically level (0 to 3% slope) areas, this variable did not play a significant role in the OCR calculation. The factors of relief and aspect can be easily incorporated into the equation.

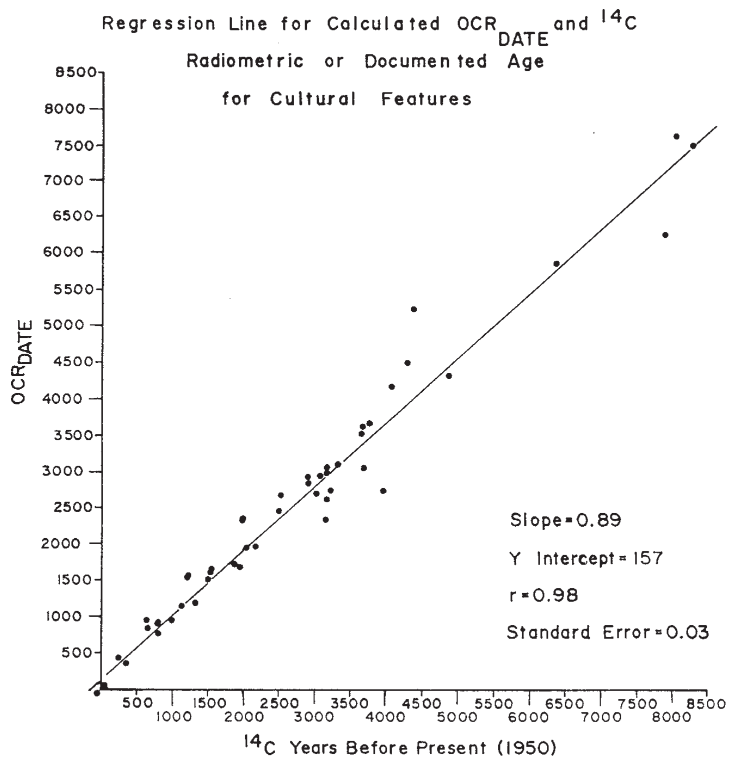

Fig. 6–1 . Correlation between known Oxidizable Carbon Ratio age estimates and known dates from earlier studies (Frink, 1994).

The equation developed for the OCR procedure may

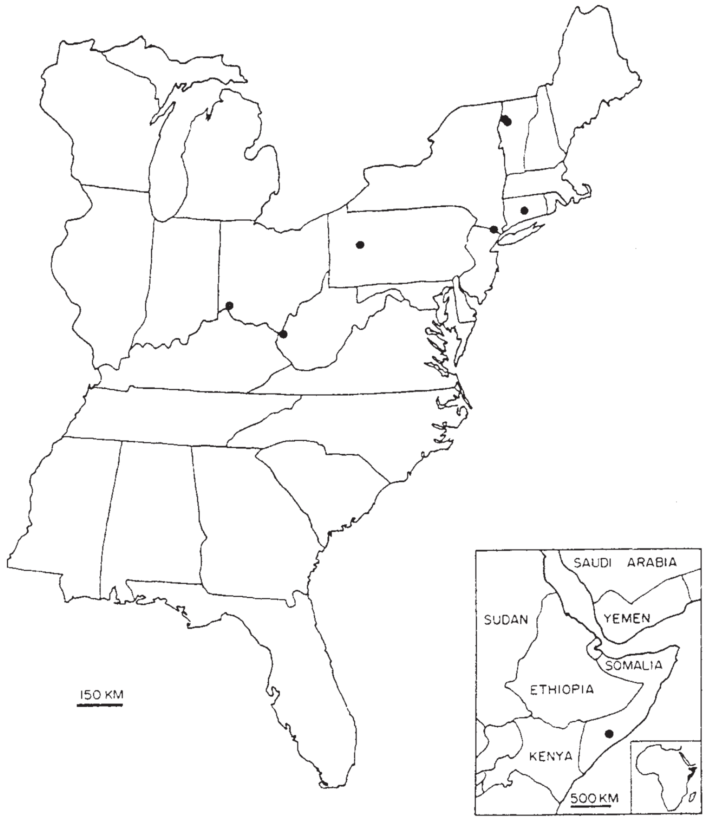

Fig. 6–2. Locations of soil samples analyzed with Oxidizable Carbon Ratio procedure in this study.

apply to other pedogenic studies. The OCR equation describes a dynamic system at the moment of analysis. Effect of changes in any one or more variables will be balanced, or distributed, throughout the system. While the OCR-dating procedure solves the equation for the variable time, the equation may be solved for each of the variables, provided that all of the other variables are known.

Materials and Methods

To demonstrate the broader archaeological and pedological applications of the OCR procedure, additional archaeological soil samples from Connecticut, Vermont, Ohio, West Virginia, Pennsylvania, New York, and from Somalia in East Africa are analyzed (Fig. 6-2). Noncultural soil samples from Ohio are analyzed to determine the age of specific soil horizons.

Soil samples of at least 100 g each were air dried prior to analyses. The samples were dried by the collectors before submission to our laboratory. Four samples, discussed in detail below, were received in moist condition.

Soil texture is determined by dry screening, with the mean texture calculated by the percentage of weight of each fraction according to USDA standard mesh screens sizes. Arbitrary values ranging from 1 (clay) through 7 (very coarse sand) are assigned to each soil fraction, and the mean weight is calculated for each sample. Soil pH is determined from a 1:1, soil/water paste. The total C is determined by the Ball Loss on Ignition procedure (Ball, 1964), and the readily oxidizable C is determined by the Walkley and Black wet combustion procedure (Walkley, 1935; Walkley & Black, 1934). As the object of analysis is charcoal, the results of the C analyses are not converted to their equivalent organic matter.

Data for the mean annual temperature and rainfall are based on National Oceanic and Atmospheric Administration (NOAA) Narrative Summaries for the period of 1941 to 1975 (Ruffner, 1978). In computing the OCR formula, the mean annual rainfall is expressed in centimeters per year, and the mean annual temperature is expressed in degrees Fahrenheit. The Fahrenheit scale is employed to accommodate pergelic and cryic soils, where the mean annual temperature expressed in degrees centigrade would require negative numbers, needlessly complicating the computations.

Although long-term fluctuations in mean annual temperatures and rainfall are common throughout the Holocene Period (10 000 yr ago to the present), their deviations from the modern mean is slight. The late Pleistocene Period, however, is characterized by several dramatic deviations from the modern mean (Mayewski et al., 1993; Taylor et al., 1993). The potential effect on the OCRDATE estimates due to climatic fluctuations during the Holocene are not expected to exceed the standard error (3%) of the estimate, and thus the modern mean annual temperature and moisture data are used without adjustments. For samples obtained from late Pleistocene contexts, however, the variables of mean annual temperature and rainfall need to be adjusted. These adjustments take the form of an estimated average temperature and rainfall based on local environmental reconstruction studies.

Results

Using the OCR procedure and the formula presented above, age estimates are obtained for 16 archaeological features containing charcoal. The resulting age estimates are compared with the expected 14C age estimates, or, when 14C data was unavailable, with temporally diagnostic artifacts (Table 6-1). Comparisons between the expected and observed age estimates for these 16 cultural features demonstrate a strong correlation (Fig.6-3).

The four outlier samples are from Connecticut and West Virginia. The two samples from Connecticut were received in moist condition. Upon inquiry, it was discovered that the soils had been stored moist on a sheltered porch for nearly 3 yr after excavation. These storage conditions increased the effects of rainfall, temperature, and soil depth. The biochemical process that the OCR procedure measures was not arrested at the time of excavation. Instead, the process was accelerated and resulted in older than expected OCRDATE estimates. Despite this fact, the degree of deviation from the expected date was nearly the same for both samples. Two samples from the site in West Virginia were sampled from periodically flooded soils. During the 19th century, log-runs on the Ohio River would jam along the sampled area leading to

Table 6–1. Contextual and chemical data from 16 cultural features and 8 soil horizons.

Location	Site number	Feature identification	Depth	Texture (mean calculated value)	pH	Expected date (yr before 1950)	^{14}C lab. number	Walkley-Black	Loss on ignition	Oxidizable carbon ratio	OCR_{DATE} (yr before 1950)
			cm					% oxidizable C	% C		
Vermont	VT-CH-569	3	32	2.32	5.1	3 060 ± 70	B-64817	0.70	2.07	2.96	3 150 ± 95
		3	29	2.5	5.2	3 060 ± 70	B-64817	0.55	1.80	3.27	3 290 ± 100
	VT-CH-613		31–40	4.06	5.0	4 000–8 000	Artifact	0.24	1.29	5.38	4 936 ± 631
			43	4.5	4.8	7 500–8 500	Artifact	0.15	1.05	7.00	7 983 ±239
Ohio	33Ha588	1	32	4.1	6.6	1 660 ± 60	B-62468	1.83	4.30	2.35	1 307 ± 39
		39	40	3.5	6.8	2 000–3 000	Artifact	1.02	2.95	2.89	2 847 ± 85
		Bt2	85	4.7	6.4	4 000–7 000	Estimate	0.59	1.65	2.80	6 069 ± 182
		Bt1	50	4.1	6.4	3 000–6 000	Estimate	0.61	2.19	3.59	4 545 ± 136
		Pleistocene	72	5.0	7.1	12 000 +	Estimate	0.11	0.61	5.55	16 404 ± 362
		Paleosol	60	5.5	7.0	8 000–18 000	Estimate	0.25	1.49	5.96	7 841 ± 235
		Bt	54	4.8	6.7	3 000–6 000	Estimate	0.37	1.71	4.62	5 869 ± 176
		Krotovina	110	5.8	6.8	8 000–18 000	Estimate	0.39	1.26	3.23	8 018 ± 241
		Bt	35	4.7	6.8	3 000–6 000	Estimate	0.43	1.71	3.98	3 303 ± 99
		Ap-B	17	4.1	6.9	200–1 000	Estimate	1.25	3.32	2.66	844 ± 25
West Virginia	Caredo	25	57.5	2.0	5.8	300 ± 90	B-62470	0.86	2.98	3.47	8 983 ± 269
		27	27.5	2.8	5.9	200–300	Estimate	0.52	1.74	3.35	3 820 ± 115
Pennsylvania	36-CL-93	27	26.45	4.1	5.8	850 ± 70	B-63150	2.04	4.57	2.24	924 ± 28
		128	22.22	4.2	5.8	850 ± 70	B-63150	1.63	4.24	2.60	911 ± 162
New York	Springhouse	13	13	6.1	5.2	270–220	Artifact	3.05	5.35	1.75	260 ±8
Connecticut	6-HT-120	Pit	30.5	2.5	6.4	685 ± 95	N/A	0.56	1.44	2.57	3 776 ± 160
		99	28.6	2.5	6.4	685 ± 95	N/A	0.61	1.84	3.02	3 681 ± 110
Somalia	Gogoshiis Qabe	GQ-1	73	5.0	7.2	9 180 ± 100	UGA-5	0.30	1.28	4.27	9 007 ± 270
		GQ-2	130	6.1	7.3	18 000 +	Estimate	0.20	0.38	1.90	11 237 ± 337
		GQ-3	75	6.1	7.2	12 915 ± 180	GX-12132	0.11	0.62	5.64	13 572 ± 407

long-term saturation of these soils. Anaerobic conditions most likely altered the rate of change in oxidizable C and led to the spurious results obtained from these samples.

The three samples from Somalia address the possible limitations of the OCR procedure on samples with a low C content and with greater age. The effect of changes in climate through time can be approximated with available paleo-environmental data (Brandt, 1985, personal communication). The Somalia samples demonstrate the viability of the OCR procedure for samples dating from the Late Pleistocene Period.

One Somalia soil sample demonstrates a significant deviation from its expected age based on its stratigraphic position and not on radiocarbon dating. The soil feature that was sampled may have been the result of bioturbation caused by rodent activity. Alternatively, the deviation from the expected age may be the result of the sample's low C content (< 0.5% total C). Normal variations in results obtained from the Walkley and Black and Ball procedures may lessen the precision of the OCRDATE estimate for samples containing low percentages of C.

Eight noncultural soil samples submitted from Ohio are analyzed to determine age estimates of specific soil horizons. Although the OCR procedure was developed to analyze charcoal, pedogenic studies using 14C analysis suggest a probable similarity between the biodegradation of charcoal and the more resistant organic matter normally found in soils. While once perceived as relatively stable, the residual organic matter undergoes degradation through time due to environmental influences (Sharpenseel, 1971; Ruhe et al., 1971; Geyh et al., 1971; Herrera &

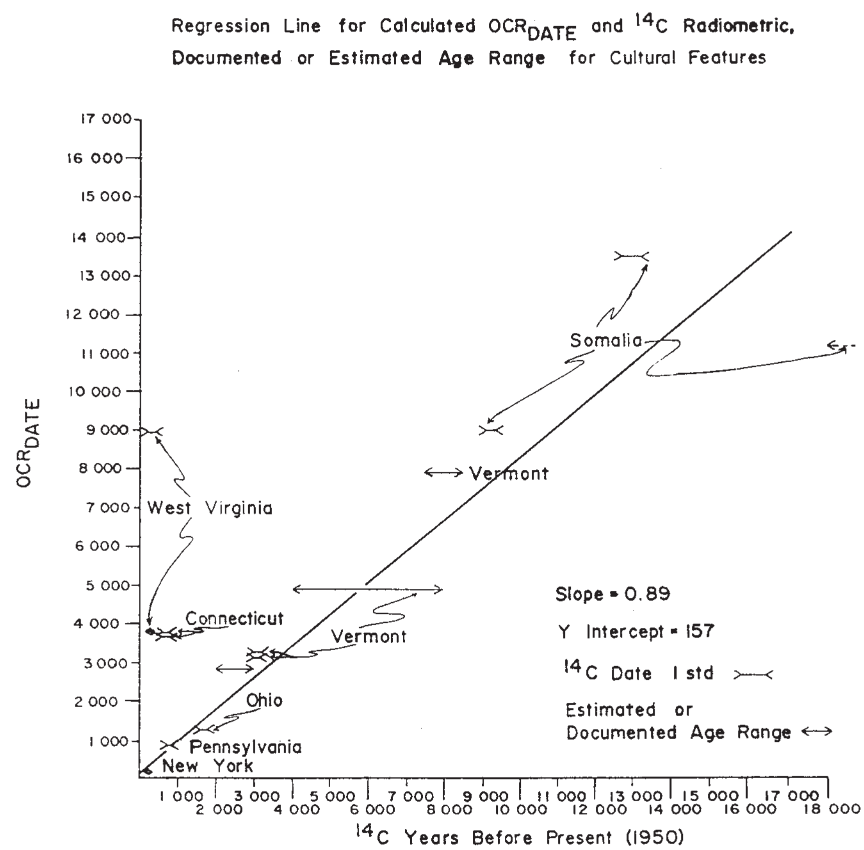

Fig. 6–3. Correlation between calculated Oxidizable Carbon Ratio OCR_{DATE} and expected age range for 16 archaeological features containing charcoal.

Tamers, 1971).

Radiocarbon age estimates obtained from the above-referenced studies were interpreted to represent the mean residence time (MRT) of the soil humus. Pedogenically active soils are constantly enriched with new residual organic matter, whereas concurrent biochemical degradation and leaching remove older residual organic matter from the soil. Both processes are environmentally dependent (Sharpenseel, 1971). The radiocarbon date of the soil horizon is an estimate of the mean age of all residual organic matter residing in the sampled soil horizon at the time of analysis.

A strong correlation between the OCRDATE estimates and the expected ages of the sampled soil horizons is evident (Fig. 6-4). As with the radiocarbon date estimates of soil horizons, the OCRDATE estimates represent a mean, not an absolute, age of the C.

Conclusion

While few people would argue that the biochemical decomposition of organic matter is independent from the environmental influences of heat, moisture, and O2, it has been argued that the process of carbonization renders organic matter inert to these influences (Dowman, 1970). The research leading to the development of the OCR-dating procedure demonstrates that C, whether in the form of fresh plant litter or charcoal, is subject to biochemical decomposition. Archaeologists who work in environments conducive to biochemical decay are familiar with this fact. Cultural features containing charcoal are common at recent open-air surface archaeological sites in the dynamic mesic and thermic environmental regimes. Few, if any, such features are found on early Holocene and late Pleistocene Period sites in similar contexts. Cultural features containing charcoal from these early periods are found only under conditions where the effects of the environment on the charcoal have been minimized. Caves and rock shelters protect features from heat and humidity, and deeply buried features are preserved by the reduction in available O2. Open-air surface areas expose archaeological sites to the full impact of the environment. Older, exposed sites lack visibly identifiable features due to the biochemical decomposition of charcoal.

The basic premise of the OCRDATE procedure, that C-containing materials decompose through time, is demonstrated by data obtained from a wide range of environmental contexts. As the process of decomposition is linear through time, the OCRDATE procedure provides an accurate age estimate for C samples by incorporating the physical and environmental contexts into the analysis.

The equation used to calculate the OCRDATE estimate describes a dynamic system similar to Jenny's (1941) model of soil genesis; that soils are the result of the interdependent dynamics of climate, biota, relief, parent material, and time. The OCRDATE equation reflects the variables of climate (mean rainfall and temperature), biota (depth below surface, percentage of C, and pH), parent material (soil texture and pH), and time. Although the variable relief did not play a significant role in these calculations, the factors of relief and aspect can be easily incorporated into the equation. The equation developed for the OCR-dating procedure may apply to other pedogenic studies. While the OCRDATE analysis solves the equation for the variable time, the equation may be solved for each of the variables, provided that all of the other variables are known.

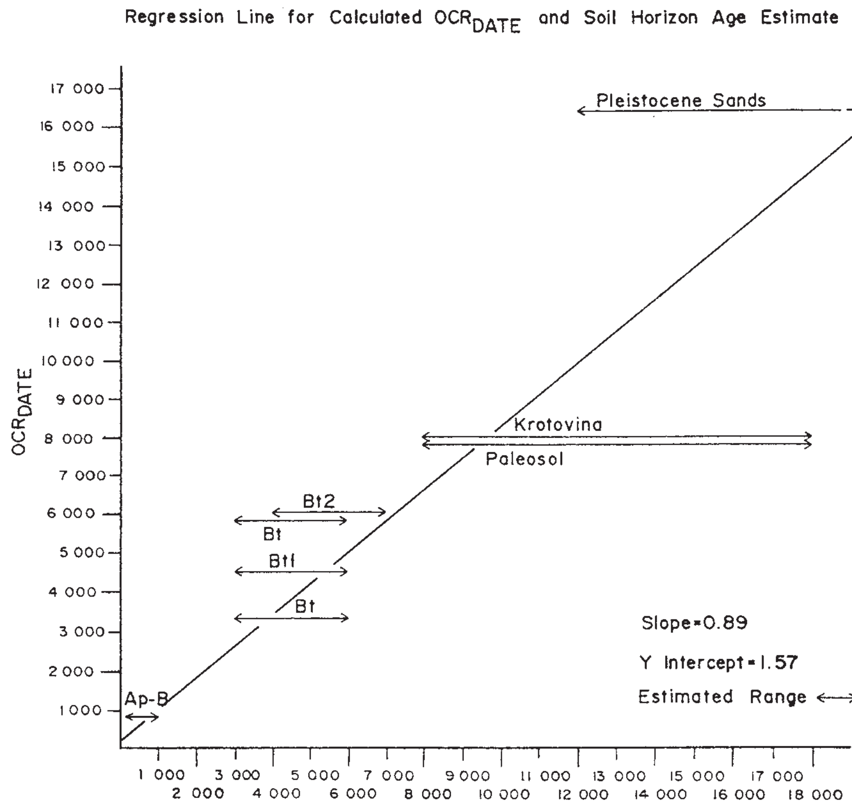

Fig. 6–4. Correlation between calculated Oxidizable Carbon Ratio OCR_{DATE} and soil horizon expected age estimate.

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