STEPPED-COMBUSTION ^{14}C DATING OF SEDIMENT: A COMPARISON WITH ESTABLISHED TECHNIQUES

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INTRODUCTION

Radiocarbon dating of bulk sediment has long been used as a method of last resort when reliable wood, charcoal, or plant macrofossils are not available for analysis. Accurate dating of sediment is complicated by the presence of multiple organic carbon fractions, each with a potentially different ^{14}C activity. Additionally, the presence of carbon bound by clay minerals can significantly reduce the accuracy of a sediment age determination, with the oldest ^{14}C ages seen in samples with the highest clay content (Scharpenseel and Becker-Heidmann 1992).

In this study we examine the usefulness of a temperature stepped-combustion technique to date sediments, similar to the method used by Delqué Količ (1995) and O'Malley et al. (1999) for dating pottery. The assumption underlying this method is that one can minimize the contribution of clay-bound carbon by combusting samples at relatively low temperatures (400 °C). The chief goal of this work is to provide comparative data between the stepped temperature approach and organic fractions isolated with established physical and chemical separation techniques. Where possible, ages from these fractions are compared with macrofossil ages.

SAMPLE LOCATIONS

Samples were obtained from three different geographic and sedimentary environments. The three sediments are from Alaska and Wyoming in the United States and the Dominican Republic. The Alaska samples are organic-rich buried soils (paleosols) from the Eva Creek formation, near Fairbanks. The Wyoming samples are alpine lake sediments from the Upper and Lower Titcomb Lakes, in the Wind River Range, Wyoming. The Dominican Republic samples are recent alluvial sediments from the Cibao valley, central Dominican Republic.

DEFINITIONS

The following operational definitions apply to the samples analyzed in this study. *AAA pretreatment* refers to the series of acid-alkali-acid (AAA) washes given to samples to remove or isolate specific fractions of carbon. Pretreatment details are given in the Sample Processing section below. *Refractory carbon* refers to carbon that derives from samples combusted at temperatures above 400 °C. *Humin* is the insoluble carbon that remains in the sediment after an AAA pretreatment. *Fulvic acid* is the organic constituent that remains in solution when a sample material is acidified. *Humic acid* is the alkali-soluble organic material removed during the second step of the AAA pretreatment. Humic acid and humin which have been isolated from samples sieved to <63µm are referred to as *<63µm humic acid* and *<63µm humin*. *Macrofossils* are identifiable pieces of plant matter large

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enough to be studied without the aid of a microscope. The term *bulk sediment* refers to largely untreated sediment that has been picked or coarsely sieved to remove modern rootlets and macrofossils before processing.

SAMPLE PROCESSING

Stepped-Combustion Bulk Sediment Fractions

The stepped-combustion method of Delqué Količ (1995) was modified at the Arizona AMS laboratory to date pottery samples (O'Malley et al. 1999) and is applied here to analyze bulk sediments. Sediments processed at the Arizona AMS lab were physically cleaned to remove rootlets, but not sieved. Bulk sediment samples processed at the U.S. Geological Survey were first sieved to <300 µm to remove the abundant macrofossils present in some of the samples. Each sediment sample was given an AAA pretreatment consisting of a 1M HCl (2 hr, 60 °C), 0.1M NaOH (overnight, 60 °C), 1M HCl (2 hours, 60 °C). Samples were placed in 9 mm Vycor combustion vessels and combusted in 0.3 atmosphere ultra-pure O_2 at 400 °C (A diagram of the extraction line is shown in Figure 1). The CO_2 produced at this step is referred to as the "low temperature humin" (LT humin) fraction. After isolating the low temperature CO_2 the remaining sample material was then pumped under a high vacuum, recharged with 0.3 atmosphere ultra-pure O_2 and heated to 900 °C. The CO_2 produced at 900 °C is referred to as the "high temperature humin" (HT humin) fraction. Both the LT and HT humin CO_2 fractions were individually passed through a platinum trap at 1000 °C to oxidize CO, a Copper Oxide/Silver trap to remove volatile gases, and two dry ice/alcohol traps at –78 °C to remove water.

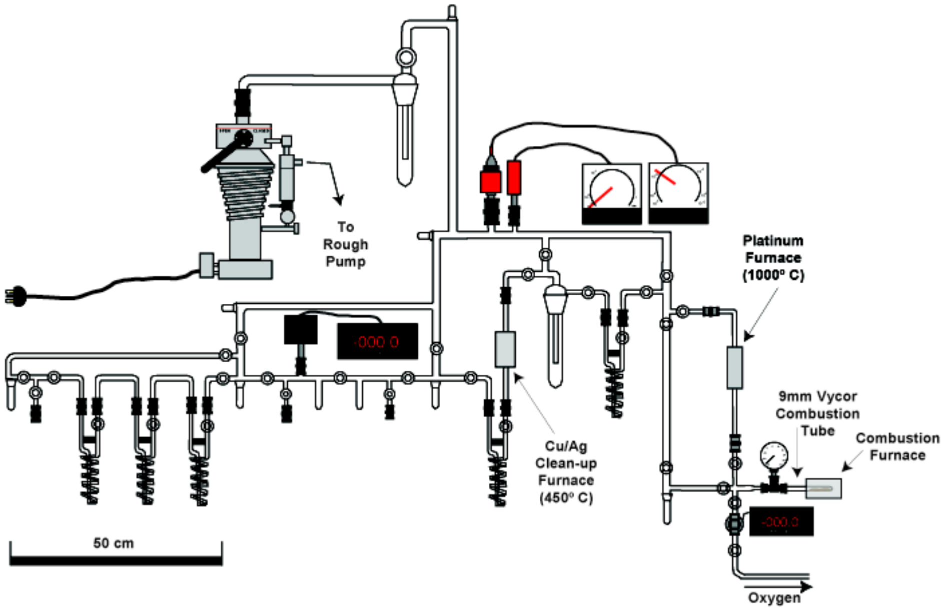

Figure 1 Stepped-combustion chamber utilized for LT and HT bulk sediment samples

Bulk Humic Acid Fractions

Bulk sediments were physically and chemically processed as above. The humic acid that came off during the alkali wash was passed through a <0.45 µm Millipore filter and re-acidified in 1M HCl to precipitate the humic acid. The solution was centrifuged, neutralized in distilled water, and dried.

<63 µm Humic Acid and Humin Fractions

The <63 µm humic acid pretreatment was modified from the procedures outlined by Abbott and Stafford (1996). Bulk sediment was dry sieved to <63 µm. The <63 µm material was next decalcified in 1M HCl (2 hr, 60 °C). Humic acid was extracted from the sediment in 0.5% KOH (4 hr, room temperature). The insoluble fraction of this solution was isolated by centrifuging. The soluble humic acid was then filtered through a 0.45 µm Millipore filter. The <0.45 µm fraction was re-acidified in 1M HCl (1 hr, room temperature) to precipitate the humic acid. This solution was centrifuged to concentrate the humic acid and remove any remaining fulvic acid. The humic acid was rinsed and centrifuged until neutral and then dried. The >0.45 µm alkali insoluble fraction, functionally defined as humin, was also re-acidified, neutralized and dried.

Plant Macrofossils

In all cases, samples of wood and charcoal were given acid-alkali-acid pretreatments.

Graphitization

Samples processed at the Arizona lab were converted to graphite over iron at 575 °C in the presence of ZnO at 425 °C. Samples processed at the U.S. Geological Survey were converted to graphite over iron in the presence of H_2 at 575 °C (Vogel et al. 1984). Graphite samples were run at the NSF-Arizona AMS facility and the Center for Accelerator Mass Spectrometry (CAMS) at Lawrence Livermore National Laboratory.

RESULTS

The results are shown in Table 1, Figure 2, and Figure 3. The relative ages of the organic fractions studied here depend upon the environment in which they formed.

Alaska Samples

The samples from Alaska range in age from about 9000 to 50,000 BP. These are organic-rich paleosols. In every case where data is available, the LT humin fraction yielded ages that were as close or closer to the macrofossil ages when compared to the other organic fractions. The LT humin and the <63 µm humic acid fractions are also in close agreement.

The largest deviation from the macrofossil ages was observed for the bulk humic acid, HT humin and the <63 µm humin fractions. In this sequence, the bulk humic acid ages are alternately older and younger than macrofossil ages. The HT humin and <63 µm humin fractions are older than the macrofossils in the first three samples. The fourth sample, AK4070, has a macrofossil age of nearly 50 ka and is considered here to be radiocarbon “dead.” The wide range of ages for all the other fractions associated with this sample may represent deficiencies in pretreatment rather than real age differences. Excluding sample AK4070, the age difference between the LT and HT humin fractions is as much as 1600 years.

Table 1 Radiocarbon measurements of all sediment fractions for the three sample suites

	Macrofossil			LT Bulk			HT Bulk			<63 µm humic acid			<63 µm humin			Bulk humic acid		
Sample ID	^{14}C age	δ^{13}C	% C	^{14}C age	δ^{13}C	% C	^{14}C age	δ^{13}C	% C	^{14}C age	δ^{13}C	% C	^{14}C age	δ^{13}C	% C	^{14}C age	δ^{13}C	% C
Eva Creek, Alaska																		
AK4015	8950 ± 60	–25	59.1	9425 ± 90	–29.1	0.1	11,115 ± 75	–27.2	0.5	9190 ± 150	–25	44.6	11,035 ± 70	–27.7	0.3	9260 ± 60	–27.7	43.8
AK4029	30,190 ± 360	–25	62.7		–27.9	0.2	32,580 ± 540	–29.2	0.3	30,660 ± 330	–27	38.8	31,730 ± 480	–27.4	0.7	25,820 ± 240	–27.2	33.1
AK4032	29,840 ± 340	–25	57.7	31,160 ± 530	–28.4	0.5	31,140 ± 440	–28.5	0.5	30,230 ± 260	–25	42.3	30,590 ± 470	–27.3	0.8	31,110 ± 460	–26.9	42.6
AK4070	49,500 ± 2700	–25	47.6	42,700 ± 1900	–27.2	0.2	34,910 ± 770	–25.7	0.2	41,300 ± 1400	–26.9	46.9	37,200 ± 1100	–26.5	0.3	42,800 ± 1800	–26.7	42.7
Cibao Valley, Dominican Republic																		
DR-1				945 ± 40	–19.9	0.1	1415 ± 70	–20.8	0.7	1760 ± 50	–16.7	9.3	2900 ± 50	–22.5	0.2			
DR-2				1765 ± 40	–14.8	0.4	1795 ± 40	–15.5	0.3	1820 ± 32	–13.6	45.7	2364 ± 37	–17.8	1.2			
DR-3				2895 ± 45	–16.7	4.2	3450 ± 85	–13.6	1.2	2915 ± 40	–14.3	24.5	4325 ± 50	–19.1	0.3	2825 ± 40	–13.7	27.7
Lake Titcomb, Wyoming																		
LT2-17	2220 ± 70	–23.1	1.8	2325 ± 50	–24.1	1.5	2625 ± 40	–30	3.7	1917 ± 53	–25.2	36.8	1785 ± 44	–25	2			
LT3-63				3750 ± 55	–23.6	0.5	4660 ± 55	–23.7	0.5									
LT3-114				3590 ± 55	–22	0.4	3900 ± 55	–20.4	0.4									
UT2-87				4845 ± 95	–23.1	0.6	5065 ± 60	–23.4	0.9									
LT3-198.5				5300 ± 60	–22.1	0.5	5380 ± 60	–23.2	1.0									
LT2-179	6210 ± 75	–24.5	1.5	6600 ± 70	–24	1.1	6630 ± 55	–24.2	1.6	6514 ± 48	–26	40.9	6603 ± 49	–25	2.5			
UT1-58				6415 ± 70	–23.5	0.7	7200 ± 65	–23.3	0.4									
LT2-210	8530 ± 80	–25.6	7	8540 ± 60	–23.7	0.6	8415 ± 60	–23.1	1.2									
LT3-298.5	9660 ± 90	–20.1	11.8	10,005 ± 65	–20.5	0.7	10360 ± 60	–21.3	0.4									
LT3-315				9820 ± 75	–20.4	0.5	9730 ± 75	–20.4	0.2									
LT2-243				9875 ± 55	–21	0.9	9865 ± 85	–21	0.5									
LT2-243.5	9700 ± 65	–22.4		10,270 ± 80	–20.4	0.5	10,330 ± 70	–20.8	0.8									
LT2-249.5	10,205 ± 70	–21.3		10,210 ± 65	–20.2	1.3	10,075 ± 90	–19.9	0.1	10,193 ± 71	–25	36.5	10,215 ± 73	–21	1.1			
LT1-256				10,245 ± 75	–20.7	0.6	10,315 ± 75	–20.3	0.3									
LT2-249.5				10,310 ± 75	–20.3	0.5	10,390 ± 75	–20.8	0.6									
LT1-257				10,520 ± 85	–22.2	0.7	10,900 ± 110	–22.5	0.4									

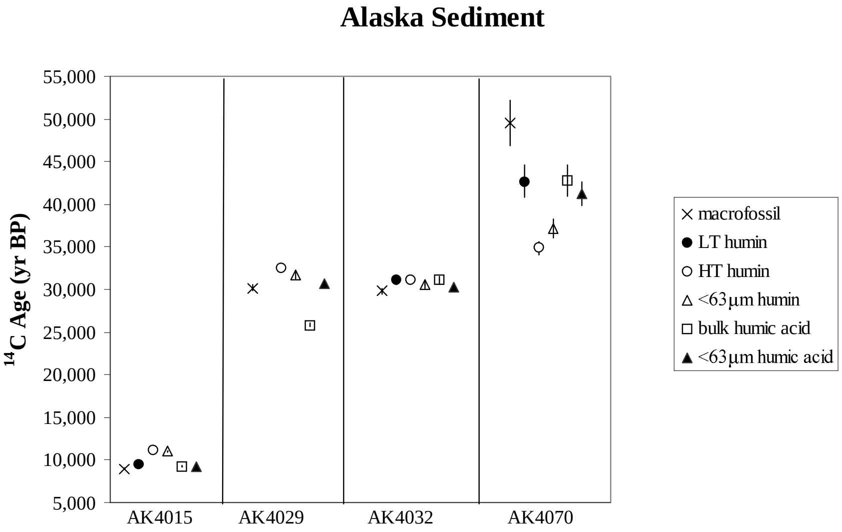

Figure 2A ^{14}C age plots for key fractions and sample intervals. Note that error bars are often smaller than the symbols.

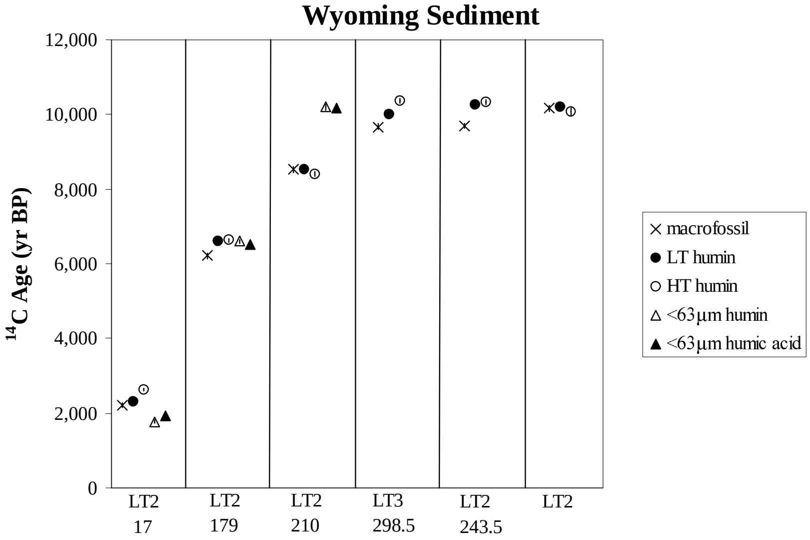

Figure 2B See Figure 2A

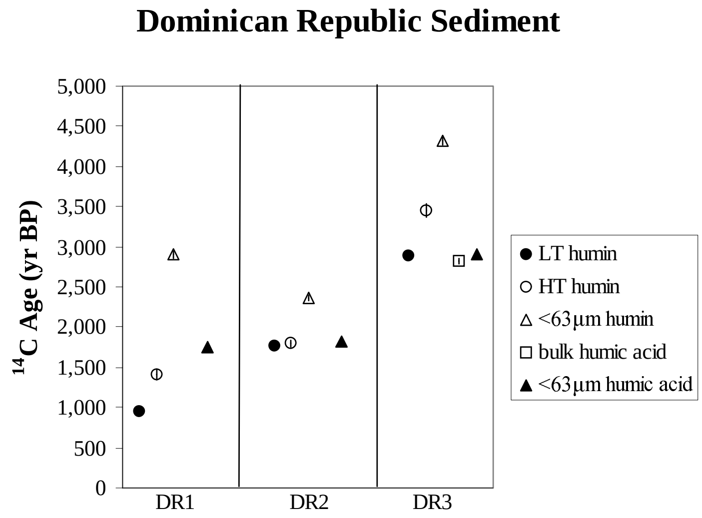

Figure 2C See Figure 2A

Wyoming samples. The samples from Wyoming range in age from about 2000 to 11,000 BP. Where data is available, the LT humin ages are as close or closer to macrofossil ages than all other fractions. Additionally, the LT humin fraction consistently yielded ages that were the same as or younger than the HT humin fraction. In this sample suite, no bulk humic acid ages were measured. The age difference between the LT and HT humin fractions is as much as 900 years.

Dominican Republic samples. The Dominican Republic samples range in age from about 1000 to 3000 BP. These are alluvial sediments in an active depositional environment. In this sample suite, no macrofossil ages were available for comparison. The LT humin fraction from all samples yielded ages that were the same as or younger than the HT humin fractions, the <63 µm humic acid fractions, and the <63 µm humin fractions. Age differences between the LT and HT humin fractions are as much as 555 years. The <63 µm humin fraction gave consistently older ages than any of the other fractions.

CONCLUSIONS

In the three sediment environments studied here, the LT humin results are close to those obtained from macrofossils and the <63 µm humic acid fraction. The bulk humic acid, <63 µm humin and HT humin fractions often give disparate ages. Figure 3 illustrates the statistical deviation of ages associated with the different fractions when compared to the generally more reliable macrofossil ages.

^{14}C ages of AAA pretreated bulk sediments incorporate carbon bound to diagenetically derived clays in the humin component. If the humin contains a large amount of clay-derived carbon in the total carbon of the sample, then it will be a significant contaminant. Where we have data, the fractions with greatest potential for contamination with clay-bound carbon (<63 µm humin and HT humin) often result in ^{14}C ages that are very different from macrofossil ages. The large differences seen in ages between HT and LT humins indicate a relatively old source of organic contamination in the sediments.

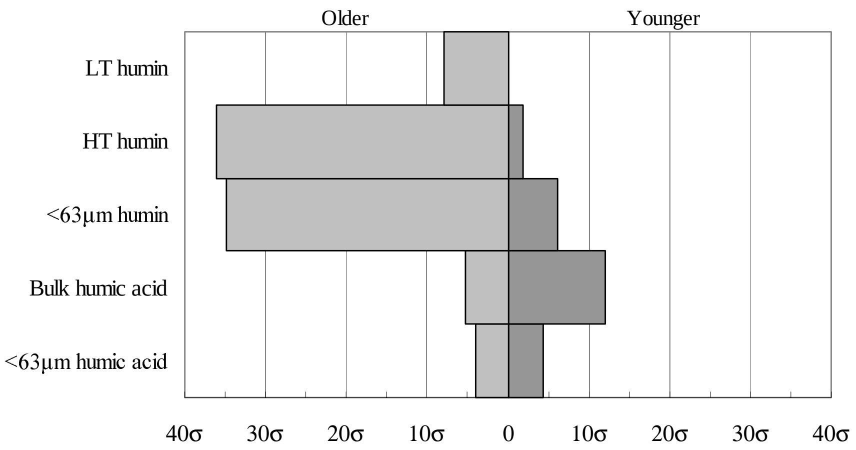

Figure 3 High-low standard deviation (σ) range from macrofossil age by fraction. Data set excludes sample AK4070.

This study is consistent with the idea that contaminating carbon associated with clay minerals can be effectively avoided with the low temperature combustion method. The technique shows promise for dating of sediments, especially where a reliable source of plant macrofossils is unavailable.

The relative ease of handling of sediment for low temperature combustion makes this technique an attractive compliment to the labor-intensive methods involved in the physical and chemical fractionation of organic compounds.

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