STEPPED-COMBUSTION ^{14}C DATING OF BOMB CARBON IN LAKE SEDIMENT

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ABSTRACT. In this study, we applied a stepped-combustion approach to dating post-bomb lake sediment from north-central Mississippi. Samples were combusted at a low temperature (400 °C) and then at 900 °C. The CO_2 was collected separately for both combustions and analyzed. The goal of this work was to develop a methodology to improve the accuracy of ^{14}C dating of sediment by combusting at a lower temperature and reducing the amount of reworked carbon bound to clay minerals in the sample material. The ^{14}C fraction modern results for the low and high temperature fractions of these sediments were compared with well-defined ^{137}Cs determinations made on sediment taken from the same cores. Comparison of "bomb curves" for ^{14}C and ^{137}Cs indicate that low temperature combustion of sediment improved the accuracy of ^{14}C dating of the sediment. However, fraction modern results for the low temperature fractions were depressed compared to atmospheric values for the same time frame, possibly the result of carbon mixing and the low sedimentation rate in the lake system.

INTRODUCTION

Accurate ^{14}C dating of lake sediment is complicated by the presence of multiple sources of organic and inorganic carbon fractions. Even after traditional acid/alkali/acid (AAA) pretreatments, radiocarbon dating of lake sediment often leads to inaccurate results because the humin component of the sediment (the fraction of humic substances that is not soluble at any pH value) includes reworked carbon adsorbed to clay minerals. In an earlier research effort, we adapted a stepped-combustion technique developed for ^{14}C dating of smoke-derived versus clay-bound carbon sources in pottery to the problem of dating sediment and paleosols (Delqué Količ 1995; O'Malley et al. 1999; McGeehin et al. 2001). In our 2001 study, we combusted sediment and paleosols at a low temperature (400 °C) to minimize the contribution of the more refractory carbon bound to clay minerals in the samples. The high temperature (900 °C) fraction was also collected and results were compared. ^{14}C ages on the low temperature fraction were in good agreement with macrofossil and humic acid ages, whereas the high temperature fraction gave disparate results.

In this study, we again applied the stepped-combustion method to dating sediment, focusing on post-bomb lake sediments with high clay and silt content, 5–35% and 50–75%, respectively (Bennett and Rhoton 2003). Abbott and Stafford (1996) suggested that in studies of lake sediments, discrete terrestrial plant macrofossils will provide the most accurate ages, followed by aquatic plant macrofossils and humic acids. Lacking sufficient quantities of macrofossils or humic acids, we instead compared ^{14}C activity of the low and high temperature combustion products of our sediment samples to ^{137}Cs bomb profile results made on the same sample material. Above-ground bomb testing during the 1950s and 1960s resulted in elevated concentrations of atmospheric ^{14}C and ^{137}Cs that peaked in 1963–1964 (Levin et al. 1985; Bergan 2002; Figure 1). Both cores taken for this study showed a strong ^{137}Cs bomb peak. We hypothesized that a ^{14}C bomb profile should be present at about the same depth as the ^{137}Cs profile if reworked carbon bound to clay in the sediment could be effectively removed from the activity of the samples.

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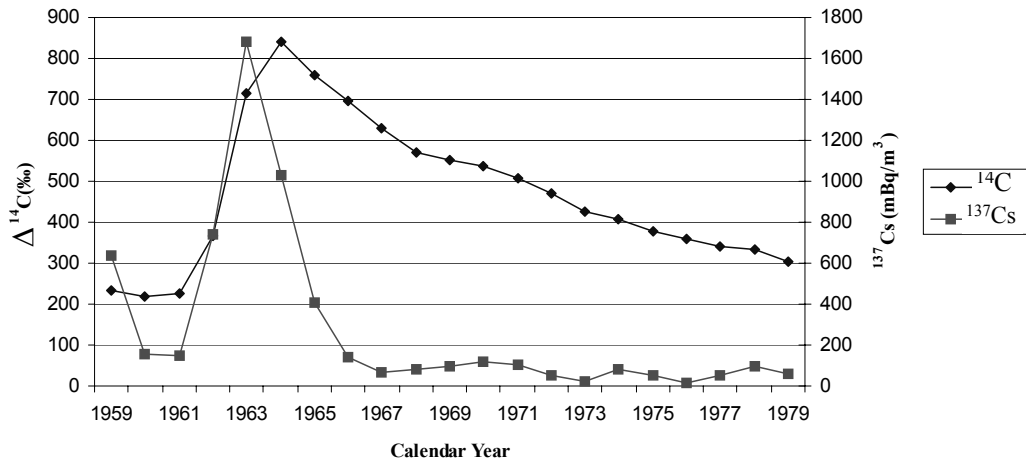[5]US Geological Survey, Atlanta, Georgia, USA.

Figure 1 Atmospheric concentrations of bomb ^{14}C and ^{137}Cs

SAMPLE LOCATION

Samples were taken from 2 sediment cores (SB-3 and SB-9) from Grenada Lake, north-central Mississippi (Figure 2). Grenada Lake is a 142-km^2 reservoir formed by the damming of the Yalabusha and Skuna rivers in the year 1954. The 2 cores were taken approximately 7 km apart within the Skuna, or northern, arm of the lake. Both cores were obtained by vibracore with minimal compaction. Core SB-3 was taken under 1 m of water; core SB-9 was taken under 2.9 m of water. Erosion, incision, and channel widening due to channelization of the rivers feeding Grenada lake have increased the sediment load to the lake since its inception. Sediment accumulation and organic content is quite variable depending on the location in the lake.
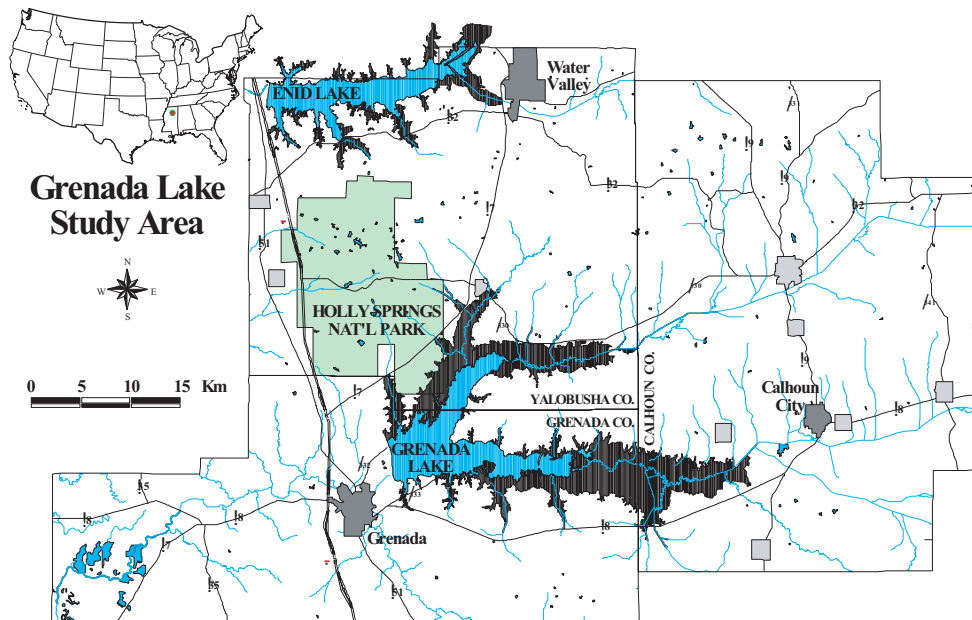

Figure 2 Map of study area, north-central Mississippi

METHODS

^{137}Cs Sample Handling

Sediment samples were cut in 2.5-cm intervals from one-half of the split cores (the other half of each core was used for ^{14}C) and shipped off to the National Oceanic and Atmospheric Administration's Great Lakes Research Laboratory for measurements. Sediment samples were weighed into vials and given a standard geometry. Samples were measured on a gamma detector. Each sample was counted for 1 day or a minimum counting error of 10%, whichever came first. Data was collected for both ^{137}Cs and ^{40}K. The counting errors for the activities of ^{137}Cs in the SB-3 core samples ranged from 3.2% to 3.9% of the reported peak activity values (defined as values with half the maximum ^{137}Cs activity or greater). Counting errors for core SB-9 were 2.9–4.8%.

^{14}C Sample Handling

Pretreatment. Sediment samples were first sieved to <63 μm to collect the silt and clay size fractions of the samples. Collecting only the fine fraction of the sediment incorporated all of the clay-bound carbon and the humic substances associated with the silt fraction, while excluding coarser disseminated fragments of plant rootlets, charcoal, etc. that would further complicate the apparent activity of each sample. The <63-μm fraction of 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 hr, 60 °C). The resultant pretreated sediment is defined here as <63 μm humin.

Stepped-combustion. 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 3). The CO_2 produced at this step is referred to as the low temperature (LT) 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 (HT) fraction. Both the LT and HT 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 2 dry ice/alcohol traps at –78 °C to remove water.
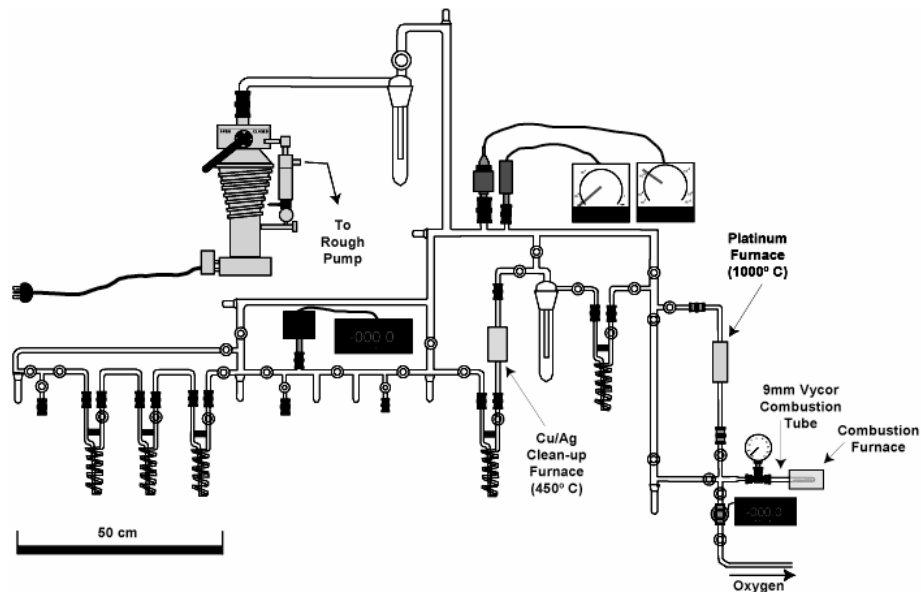

Figure 3 Diagram of the extraction line

Graphitization. Samples were converted to graphite over iron at 575 °C in the presence of ZnO at 425 °C.

AMS Dating. The samples were physically and chemically processed and the ^{14}C activities measured at the NSF-Arizona AMS facility in Tucson, Arizona.

RESULTS AND DISCUSSION

Notation

All of the results in this study are given as fraction modern carbon (*F*). *F* is defined as

$$F = (^{14}C/^{13}C)_s \,/\, (^{14}C/^{13}C)_{std} \tag{1},$$

where $(^{14}C/^{13}C)_s$ is the sample ratio and $(^{14}C/^{13}C)_{std}$ is the calculated standard ratio at 1950, determined from measurements of NBS oxalic acid standards with both ratios normalized to $\delta^{13}C = -25‰$ (Donahue et al. 1990).

The <63-μm low temperature and high temperature humin samples are referred to and showed graphically as LT and HT, respectively. The combined activity of a sample, which was calculated from the relative input of both the LT and HT fraction modern values, is referred to and shown graphically as "Combined."

Core SB-9

Results for core SB-9 are given in Table 1 and shown graphically in Figure 4a. A strong ^{137}Cs peak is evident in the core at a depth of 74.2 cm. Using the 1963 ^{137}Cs peak as a marker, the sedimentation rate for this site is 1.85 cm/yr. Organic carbon concentrations are low, ranging from 0.12–0.43% in the LT fraction and 0.08–0.28% in the HT fraction. The ^{14}C activity of the stepped-combustion products demonstrate the disparity of results that can occur from fractionating sediment by temperature of combustion. The LT fraction for sediment samples from core SB-9 show a weak but recognizable bomb curve with a peak (*F* = 1.0946) at 63.4 cm. The HT fraction for samples at all depth intervals have *F* values well below 1.0. In every case, LT samples have older HT counterparts indicating ^{14}C ages that range from a few hundred to as much as 1800 BP. The Combined activity values for the SB-9 core show a single bomb ^{14}C sample with *F* = 1.0416 at 63.4 cm.

Core SB-3

Results for core SB-3 are given in Table 1 and shown graphically in Figure 4b. A ^{137}Cs peak is evident in the core at a depth of 23.8 cm. The sedimentation rate of 0.6 cm/yr based on this 1963 peak is considerably lower than with core SB-9. Organic carbon concentrations are very low, ranging from 0.03–0.29% in the LT fraction and 0.02–0.20% in the HT fraction (based on the CO_2 yield of each fraction relative to the total yield). As with core SB-9, the data show a substantial offset between *F* values for the LT and HT fractions. HT fractions consistently give older results by as much as 7000 ^{14}C yr BP. There is only 1 sample indicating the presence of bomb carbon (*F* = 1.0612). It occurs in the LT fraction at a depth of 23.8 cm, matching the peak for the ^{137}Cs curve.

The Bomb Profiles

For core SB-9, the 63.4 cm ^{14}C bomb peak in the LT fraction appears to be 10.8 cm shallower than the ^{137}Cs peak at 74.2 cm. The difference may be less if we consider the statistical overlap of [14]C *F* values for samples at the 63.4 cm and 66.1 cm intervals. Core SB-9 has a high sedimentation rate.

Table 1 Results for core SB-3.

| Core ID	Core depth midpoint (cm)	^{137}Cs (dpm/g)	+/-	AMS ID	^{14}C activity (F) LT fraction F	+/-	δ^{13}C	HT fraction F	+/-	δ^{13}C	Combined F	+/-	% Carbon LT	HT	Combined
SB9-21	55.3	0.818	0.081	AA55361	1.0065	0.0052	−26.4	0.9038	0.0103	−25	0.9736	0.0068	0.4	0.19	0.59
SB9-22	58.0	0.998	0.081	AA55362	1.0502	0.0044	−26.7	0.8958	0.0054	−25	0.9766	0.0049	0.3	0.28	0.58
SB9-23	60.7	1.076	0.083	AA55363	1.0516	0.0045	−26.4	0.7968	0.0060	−25	0.9814	0.0049	0.43	0.16	0.59
SB9-24	63.4	1.577	0.084	AA55364	1.0946	0.0068	−26.6	0.9013	0.0052	−25	1.0416	0.0064	0.31	0.12	0.43
SB9-25	66.1	1.466	0.069	AA54269	1.0818	0.0051	−28.2	0.9142	0.0041	−25.8	1.0069	0.0047	0.14	0.11	0.25
SB9-26	68.8	1.682	0.088	AA54270	1.0579	0.0063	−27.4	0.9189	0.0045	−26.2	0.9964	0.0055	0.15	0.12	0.27
SB9-27	71.5	2.546	0.074	AA54271	1.0061	0.0043	−27.7	0.8749	0.0048	−27.1	0.9607	0.0045	0.12	0.07	0.19
SB9-28	74.2	3.459	0.104	AA54272	0.9170	0.0040	−28.6	0.8543	0.0040	−27.1	0.8816	0.0040	0.16	0.21	0.37
SB9-29	76.9	2.996	0.087	AA54273	0.9727	0.0044	−27.8	0.8946	0.0040	−27.3	0.9290	0.0041	0.23	0.29	0.52
SB9-30	79.6	1.936	0.092	AA54274	0.9132	0.0039	−28.3	0.8231	0.0039	−28.2	0.8636	0.0040	0.14	0.17	0.31
SB9-31	82.3	0.390	0.076	AA54275	0.9443	0.0042	−28.3	0.7898	0.0046	−26.7	0.8852	0.0044	0.13	0.08	0.21
SB3-3	6.3	0.286	0.056	AA55974	0.8252	0.0102	−26.97	0.3479	0.0111	−25	0.7440	0.0104	0.10	0.02	0.12
SB3-4	8.8	0.371	0.066	AA55975	0.8247	0.0127	−27.58	0.4707	0.0084	−25	0.6478	0.0106	0.04	0.04	0.08
SB3-5	11.3	0.449	0.074	AA55976	0.8166	0.0106	−26.06	0.4420	0.0129	−25	0.6930	0.0114	0.06	0.03	0.09
SB3-6	13.8	0.408	0.078	AA55977	0.8612	0.0107	−26.87	0.6137	0.0086	−25	0.7548	0.0098	0.08	0.06	0.14
SB3-7	16.3	0.322	0.077	AA55978	0.7866	0.0121	−27.20	0.3231	0.0091	−25	0.6012	0.0109	0.03	0.02	0.05
SB3-8	18.8	0.675	0.06	AA55979	0.9492	0.0129	−28.01	0.7323	0.0099	−25	0.8559	0.0117	0.12	0.09	0.21
SB3-9	21.3	0.775	0.078	AA55980	0.9141	0.0109	−27.24	0.5143	0.0080	−25	0.7982	0.0100	0.10	0.04	0.14
SB3-10	23.8	2.407	0.094	AA55981	1.0612	0.012	−27.31	0.9113	0.0104	−25	0.9947	0.0113	0.22	0.18	0.40
SB3-11	26.3	2.179	0.069	AA55982	0.9611	0.011	−28.97	0.8363	0.0097	−25	0.8988	0.0103	0.20	0.20	0.40
SB3-12	28.8	0.271	0.069	AA55983	0.923	0.0106	−28.09	0.7956	0.0092	−25	0.8810	0.0101	0.29	0.14	0.43
SB3-13	31.3	0.011	0.078	AA55984	0.9214	0.0108	−27.72	0.8168	0.0104	−25	0.8837	0.0106	0.21	0.12	0.33

Grenada Lake (SB-9)
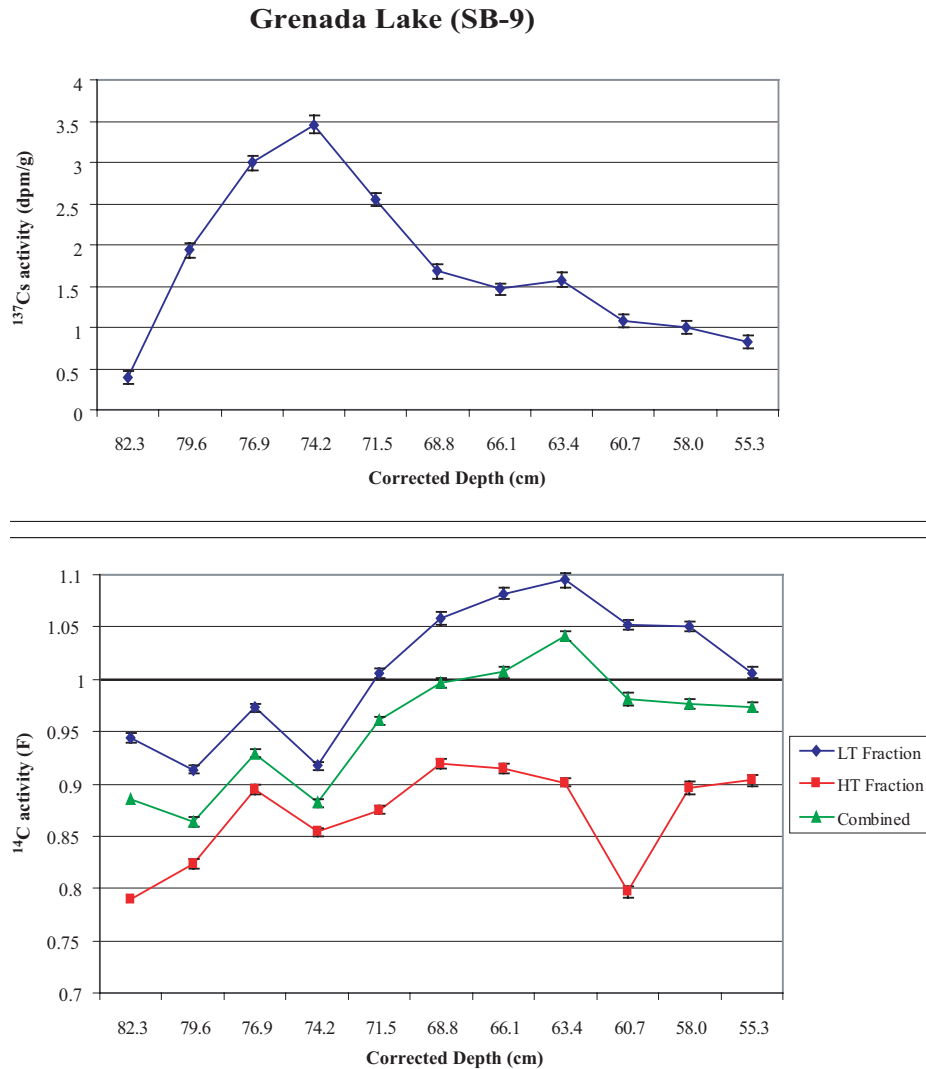
Figure 4a ^{14}C and ^{137}Cs activity versus depth for core SB-9

Using the ^{137}Cs 1963 peak as a marker, sediment is accumulating in the core at a rate of 1.85 cm/yr. This sedimentation rate translates to a offset of 4.5–5.8 yr between the ^{14}C and ^{137}Cs peaks. It is reasonable to assume that the ^{14}C bomb peak would develop somewhat later than the ^{137}Cs peak in lake sediment since cesium is deposited directly through atmospheric fallout, whereas bomb carbon must be incorporated as biomass before being diagenetically altered and deposited as sediment in the lake reservoir.

In core SB-3, the single ^{14}C bomb carbon value in the LT fraction does appear to match up with the ^{137}Cs peak. However, peak values for ^{137}Cs overlap at the 2-σ level for the 23.8-cm and 26.3-cm intervals. With a sedimentation rate of just 0.6 cm/yr, the ^{14}C peak may have developed a few yr later than the ^{137}Cs peak, as with core SB-9.

For both core SB-9 and SB-3, ^{14}C *F* values in the 1950s and 1960s bomb carbon timeframe are significantly depressed relative to atmospheric concentrations of carbon for the same period. The LT
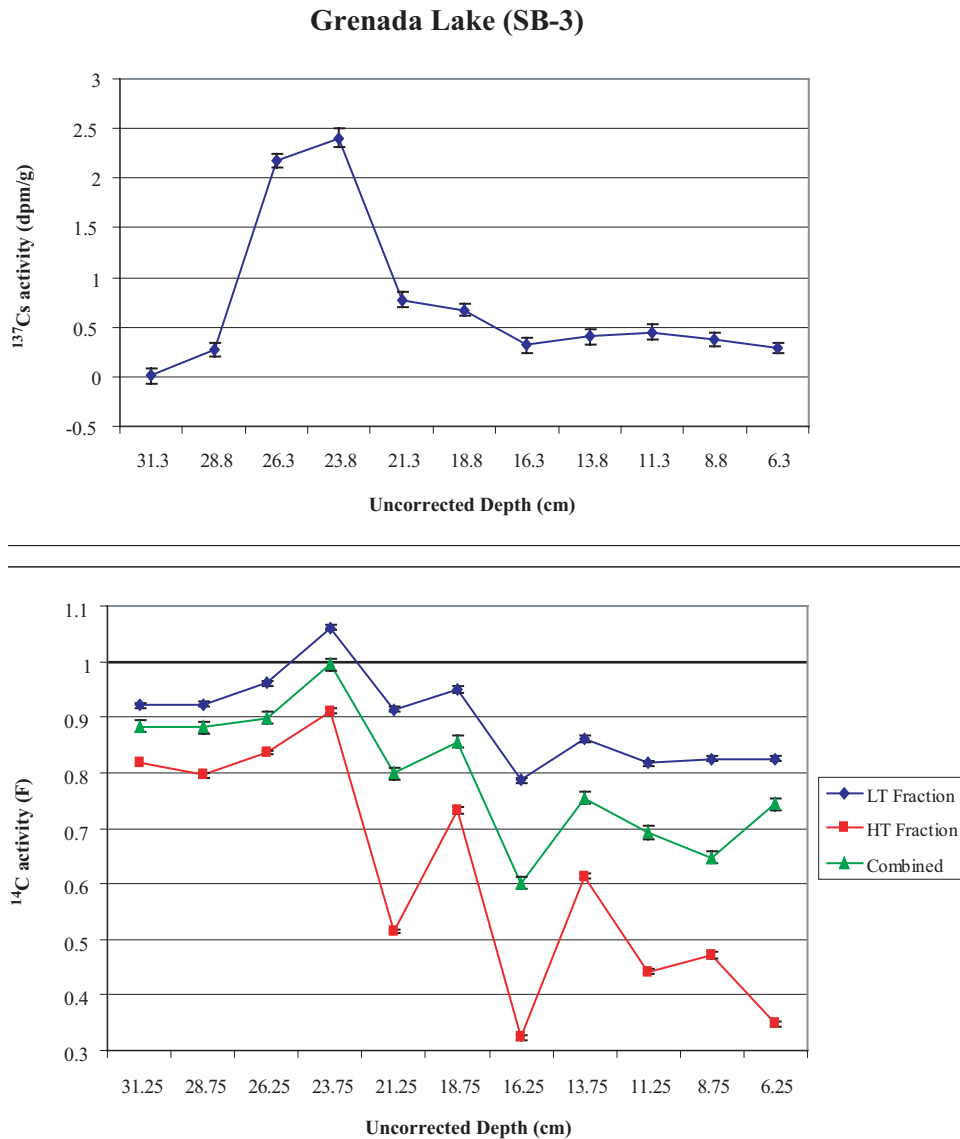
Grenada Lake (SB-3)

Figure 4b ^{14}C and ^{137}Cs activity versus depth for core SB-3

combustion of these sediments has improved the accuracy of the ^{14}C results. However, ^{14}C *F* values are still too low. This is probably caused by a mixing process where various pools of carbon of differing ages combine, resulting in an apparent age for the sediment. The effect on an apparent age is more pronounced for core SB-3 than SB-9. The low sedimentation rate of core SB-3 means that surface sediment was slow to be buried, likely resulting in greater mixing of carbon and depressed ^{14}C *F* values for the selected samples. ^{137}Cs is not affected by diagenetic forces and, thus, sample activities are unlikely to be affected by the apparent age problem.

By holding the sampling intervals constant for both cores, the low sedimentation rate of core SB-3 relative to SB-9 would also work to reduce ^{14}C *F* values in SB-3. A low sedimentation rate increases the number of years represented in a segment and, as a direct result, the activity measured for that

segment. This effect is also seen for the ^{137}Cs peaks of the cores. The peak ^{137}Cs activity value for core SB-3 is lower than that of SB-9, as it is for ^{14}C.

While the HT fraction is consistently older than the LT fraction in the 2 cores, there appears to be a correlation between the activities of both temperature fractions with depth at various places in the cores. Note the jump in activity for both the LT and HT fractions in core SB-9 at 76.9 cm and the depression of the LT and HT fractions in core SB-3 at 16.3 cm. This may reflect bleeding of carbon from 1 temperature fraction to the other. It is possible that old, reworked carbon is being incorporated into the LT fraction at a lower temperature than expected. Conversely, some of the labile carbon may combust at a slightly higher temperature than the 400 °C of our LT combustions. A more thorough calorimetric study involving additional temperature fractions (e.g. 50 °C intervals) should improve our understanding of temperature effects in the ^{14}C activity of sediment.

CONCLUSIONS

A ^{14}C bomb curve profile in sediment can be a useful tool to help establish sedimentation and carbon sequestration rates, especially when reliable plant macrofossils are absent. However, older reworked carbon adsorbed to clay minerals can mask the true ^{14}C activity of the sediment, unless it can be effectively removed from the sample during processing.

Through the use of a stepped-combustion approach for ^{14}C dating, we have shown that low temperature combustion of sediment improves the accuracy of the results by removing older, reworked carbon bound to clay. Fraction modern values for the LT fraction of these sediments are depressed relative to atmospheric concentrations for the same timeframe. This may reflect mixing of various pools of carbon in the lake environment. Core SB-3 is depressed even more than SB-9, as evidenced by ^{14}C and ^{137}Cs peak activities. This probably reflects the effect of a constant sampling interval on cores with markedly different sedimentation rates.

For cores SB-9 and SB-3, the refractory carbon associated with clay minerals that was isolated during the high temperature combustion was considerably older than the labile carbon fraction associated with the low temperature combustion. Both cores showed evidence of bomb carbon primarily in the low temperature fraction as expected. Peak values of bomb ^{14}C occur stratigraphically at or slightly above the ^{137}Cs peak in both cores, probably reflecting a lag time for incorporation of plant-derived carbon in sediment.

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