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DEVELOPMENT OF A ROBUST ^{14}C CHRONOLOGY FOR LYNCH'S CRATER (NORTH QUEENSLAND, AUSTRALIA) USING DIFFERENT PRETREATMENT STRATEGIES

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ABSTRACT. Lynch's Crater in northeastern Australia provides a long, continuous record of environmental change within the Late Quaternary. Here, we present newly determined radiocarbon ages, using acid-base-acid stepped combustion (ABA-SC) and acid-base-wet oxidation stepped combustion (ABOX-SC) pretreatment strategies. The new results largely confirm the original untreated radiocarbon results for the uppermost 9 m of sediments, (ca. 35 ka BP). Below this depth, results from both pretreatment methods are in stratigraphic agreement and extend the dating of the record from 38 ka BP to about 48 ka BP, although an apparent increased sedimentation rate below 12 m is questionable. The scarcity of "charcoal" in several of the samples raises questions regarding the application of ABOX-SC to lake or swamp sediments, with evidence for contributions from younger, chemically resistant bacterial carbon along with fine "charcoal" in some samples. However, the extent to which this phenomenon is significant to the final age estimate appears to be sample specific, and is probably dependent upon the length of the wet oxidation step in the pretreatment.

INTRODUCTION

The continuous sequence from Lynch's Crater (17°37′S, 145°70′E) on the Atherton Tableland (Figure 1) provides the main reference for Late Quaternary environmental change in north-eastern Australia with one of the most complete environmental records of the last two glacial-interglacial cycles in Australia (Kershaw 1974, 1976, 1978, 1986). The crater, which is of volcanic origin, contains at least 60 m of lake and peat sediments, and records significant vegetation change in response to climatic oscillations as well as more sustained changes in taxon and community distributions, possibly resulting from Aboriginal activity in the area (Kershaw 1986). It is important to produce an accurate chronology for the sequence in order to determine those global and regional factors forcing change and to provide a more robust age for possible early human impact in the area.

The original chronology was based upon 10 bulk radiocarbon ages derived from the uppermost 9 m of sediments and it was necessary to estimate the age below this depth by extrapolation, assuming linear sedimentation and taking into account the moisture content of the sediments (Kershaw 1980). More recently, an attempt to derive a reliable chronology was made using a general correlation with an oxygen isotope and ^{14}C dated marine palynological record (ODP-820) from the continental slope adjacent to the Atherton Tableland (Figure 1) (Moss and Kershaw 2000), though the possibility of significant hiatuses in the ocean core makes the correlation uncertain.

Terrestrial plant macrofossils are considered to be the most reliable dating material for [14]C (Törnqvist et al. 1992; Björck et al. 1998; cf. Turney et al. 2000). However, dating of such material was not possible at Lynch's Crater, where few such macrofossils are preserved in the sediments. One alternative is the use of an ABA pretreatment on bulk sediments, believed to remove the majority of younger contaminants and therefore provide reliable age estimates to at least 30 ka (e.g. Longmore and Heijnis 1999). In most cases, ABA pretreatment is all that is required to remove contaminants

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and provide reliable age estimates. However, it has been demonstrated that in certain environments the ABA pre-treatment does not remove all contaminants (e.g. Gillespie et al. 1992; Gillespie 1997). This becomes particularly critical as the age of the sample increases. The difficulty of ensuring that ages are reliable at <1% modern carbon levels has hindered progress in a range of studies from many disciplines (cf. Allen and Holdaway 1995; Chappell et al. 1996).
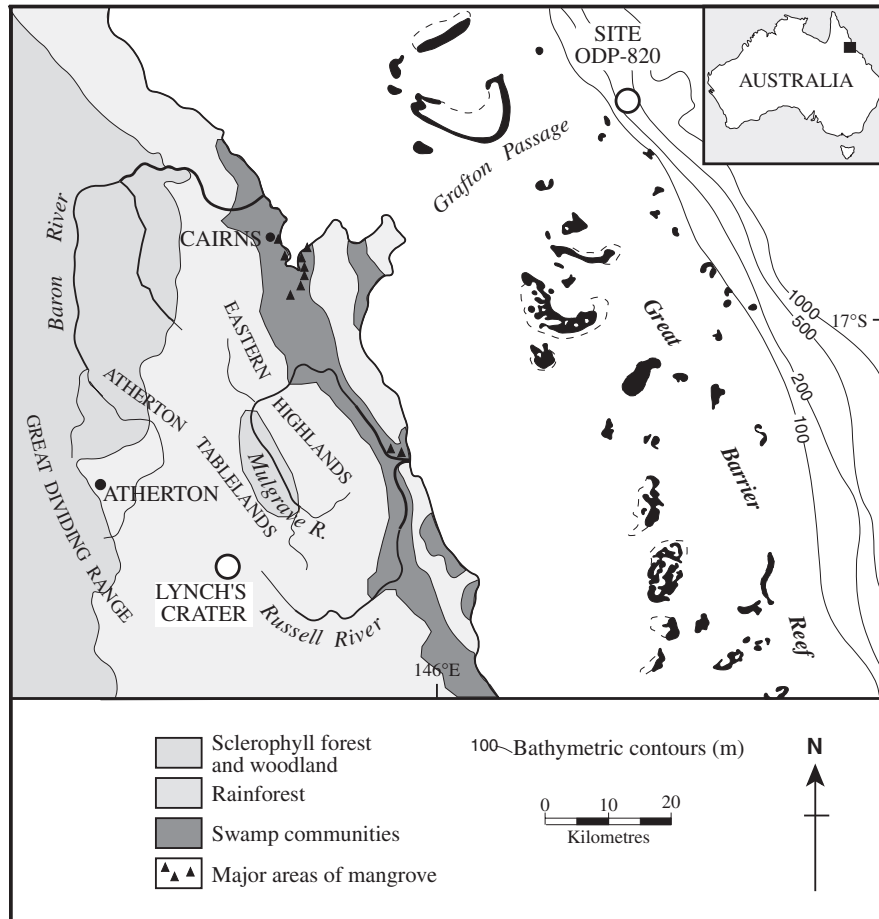

Figure 1 Location of Lynch's Crater within northeastern Australia

Minimizing modern carbon contamination is particularly relevant to Lynch's Crater, where there is considerable interest in a marked increase in "charcoal" particles at around 9 m ("charcoal" is defined here as a generic term for burnt wood of different chemical structure and properties) due to the proposed relationship with human activity in the catchment. Conventional liquid scintillation ^{14}C dating of bulk sediments with no pretreatment (Kershaw 1976, 1978, 1986) placed this transition at around 38 ka BP, which is very close to the presumed limit of the method at this time. Recently, a stringent pretreatment regime has been developed for charcoal, and this has been shown to permit reliable dating of charcoal fragments back to at least 50 ka BP (Bird et al. 1999). The method consists of an acid-base-wet oxidation chemical pretreatment, followed by stepped combustion (ABOX-SC) of the resulting material, and eliminates all material except chemically-resistant charcoal. For

charcoal, it appears to be superior to the more conventional ABA pretreatment, even when the latter is combined with stepped combustion. To date, however, the ABOX-SC technique has been applied only to hand-picked charcoal from terrestrial sites, and it is not clear that it would be equally applicable to samples from a lacustrine or swamp environment where only very fine "charcoal" is present. Further, the fine "charcoal" in Lynch's Crater sediments represents only a small fraction of the total organic carbon, so the potential for contamination of the "charcoal" (and possibly vertical movement) is greatly increased.

The purpose of this study is therefore threefold:

1. To determine whether the original chronology reported for Lynch's Crater is reliable.
2. To determine whether the ABOX-SC or ABA-SC method is the more reliable technique for the analysis of fine organic-rich sediments.
3. To extend the chronology of the Lynch's Crater site beyond the present limit set at 9m in the original core.

METHODS

Insufficient core material remained from the original work and it was necessary to recore the site (as close as possible to the original coring locations). This was carried out using a modified Livingstone sampler in November, 1998 (Figure 2). 1 m sections were individually wrapped in the field and stored at 4 °C. A detailed lithostratigraphy, using a modified Troels-Smith system (Kershaw 1997) was undertaken in the laboratory.

To aid comparison with the original chronology, organic carbon content was determined at 10 cm intervals throughout the entire core using an elemental analyzer. All samples were acid washed with 10% HCl prior to measurement.

The original ^{14}C chronology reported for the sequence was based upon untreated bulk organic peat and lake sediments. We undertook ABA and ABOX pretreatments on bulk sediment samples, following wet sieving through mesh size 2 mm to remove extraneous root material. The ABOX pretreatment is a modification of Bird and Gröcke (1997) and is described in detail in Bird et al. (1999). The technique involves the sequential pretreatment of samples with HCl, HF and NaOH followed by a $K_2Cr_2O_7/H_2SO_4$ oxidation at 60 °C. Although it is possible to leave bulk charcoal in the oxidation stage for 14 hr or longer, no sediment was oxidized for this length of time as the $K_2Cr_2O_7/H_2SO_4$ was observed to oxidize the samples extremely rapidly. As a result, the maximum time samples were left to oxidize was 7 hr, though this was sample dependent, and in some instances was as short as 2 hr. Results from macroscopic charcoal have shown that consistent, reproducible ages can be obtained from combustion at 850 °C, and that lower temperature fractions may still contain younger carbon (Bird et al. 1999). Thus, although stepped combustion of the ABOX pretreated samples was undertaken at 330, 630 and 850 °C, graphite targets for accelerator mass spectrometry (AMS) were produced only from the CO_2 evolved at the highest temperature step. Parallel samples were also prepared using the ABA methodology, in which the final oxidation step is replaced with a simple HCl treatment. Again, a stepped combustion procedure was employed and only the CO_2 evolved at 850 °C was used to produce graphite for AMS. Due to the paucity of material following pretreatment and graphitization, a δ^{13}C of –25‰ was assumed (any deviation from the assumed δ^{13}C values is considered here unlikely to have a significant influence on the ages reported here as a shift in δ^{13}C of 1‰ is equivalent to 16 ^{14}C years). Bird et al. (1999) have shown that the stepped combustion procedure can also substantially reduce backgrounds for ABA-treated charcoal samples. The ^{14}C contents of the graphite targets were measured by AMS using the 14UD ANU accelerator in the Department of Nuclear Physics at the Australian National University (laboratory code ANUA-) (Table 1).

In order to determine our ^{14}C backgrounds for these procedures, samples from a depth of 20 m in the original core (considered to be "[14]C-dead") were processed in the same way as above. However, owing to the small sample sizes resulting from both pretreatment methods it was necessary to combine the CO_2 evolved at the 630 and 850 °C steps for graphitization.

Lithostratigraphy and Core Correlation

The stratigraphy of the uppermost 16 m sediments is given below. The scale for sediment characteristics and components is 0 to 4, with 4 representing the lowest value or absence and 4 representing the highest value or maximum representation.

0–2.14 m	Black partially decomposed fibrous detritus with long roots in the uppermost 50 cm (darkness 4, stratification 0, elasticity 4, dryness 2, herb detritus 2, humus 2, silt +).
2.14–4.06 m	Brown (black when oxidized) decomposed detritus (darkness 4, stratification 0, elasticity 4, dryness 2, homogenous, upper boundary 2, humus 3, herb detritus 1, silt +).
4.06–7.00 m	Brown (black when oxidized) fibrous detritus (darkness 4, stratification 0, elasticity 4, dryness 2, upper boundary 2, herb detritus 2, humus 2, fine detritus +).
7.00–12.26 m	Brown (black when oxidized) fibrous detritus (darkness 4, stratification 0, elasticity 4, dryness 2, upper boundary 2, humus 3, herb detritus 1, fine detritus +).
12.26–12.80 m	Brown (black when oxidized) organic lake mud with detritus component (darkness 4, stratification 0, elasticity 4, dryness 2, upper boundary 1, herb detritus 1, organic lake mud 1, humus 1, clay 1). Transitional.
12.80–14.00 m	Brown (black when oxidized) homogenous lake mud (darkness 4, stratification 0, elasticity 4, dryness 2, upper boundary 2, organic lake mud 2, herb detritus 1, clay 1).
14.00–15.93 m	Brown (black when oxidized) homogenous lake mud (darkness 4, stratification 0, elasticity 4, dryness 2, upper boundary 2, organic lake mud 2, clay 2, herb detritus +).

The organic carbon content largely mirrors the above stratigraphy but provides additional lithostratigraphic information for the correlation between cores (Figure 3). The pattern of variation in the organic carbon content is virtually identical to that of the original organic matter content determined by Kershaw (1976) and allows precise comparison between the original chronology and the new ^{14}C ages (Figure 3).

RESULTS

The new ABA-SC ^{14}C ages are largely in stratigraphic order. Under the assumption that the value of 0.20 pMC measured for the 20 m sample represents background, these ages range from around 9600 BP at 1.55 m to around 48,000 BP at 15.9 m (Table 1). In contrast, the supposed background value from the ABOX-SC pretreated 20 m sample is 0.67 pMC (approximately equivalent to 40,000 BP), which is significantly higher than the value of 0.23 pMC obtained for the 14.45 m sample (ANUA-13406, Table 1), suggesting that the background through the sequence for ABOX-SC pretreated samples may be more variable than the ABA-SC pretreated samples.

The "charcoal" content of the Lynch's Crater sediments is negligible below 10.75 m and variable above this depth (Kershaw 1986; Turney et al., in preparation). By definition, ages obtained from

samples pretreated using ABOX measure the ^{14}C activity of chemically-resistant charcoal. However, the relatively high ^{14}C activity (using ABOX-SC) at 20 m is almost certainly due to the necessity of combining the 630 and 850 °C fractions from sediments that contain little or no "charcoal". Support for this possibility is provided by separate measurements on the ABOX-SC 630 and 850 °C graphite targets from 15.90 m (ANUA-13402 and –13403), which record a significant difference in ^{14}C content between the two fractions (3.69 and 0.64 pMC respectively, Table 1). A value of 0.20 pMC has therefore been used as the "best-case scenario" background value for both pretreatment methods.
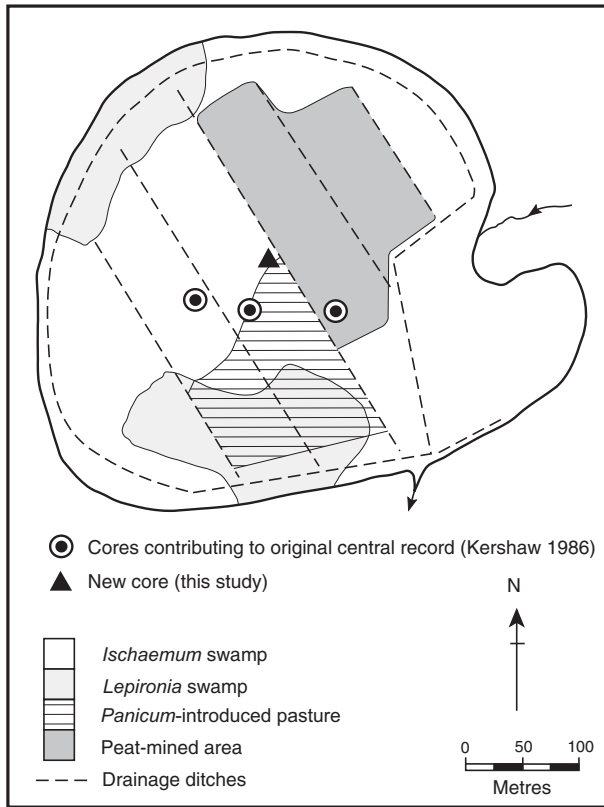

Figure 2 Location of the newly taken core and the original cores used by Kershaw (1986)

DISCUSSION

Using this approach, the oldest ABOX-SC age distinguishable from background is 44,000 BP at 15.90 m, though at depths below 10.75 m, the ABOX-SC ages should be treated as minimum ages (Table 1).

The newly determined ^{14}C ages (Table 1) are consistent with the original ages (Figures 3 and 4). With the exception of one of the original ages at 5.3 m, the ^{14}C measurements determined from the uppermost 9 m from untreated samples and reported by Kershaw (1976), are largely in agreement with the ABA-SC and ABOX-SC results. Due to the relatively high background reported for the original chronology (equivalent to ca. 40,000 BP), an almost linear sedimentation rate was suggested by the original chronology to this depth (Figure 4). However, the newly combined ^{14}C dataset suggests that just beyond the depth at which background values for the untreated samples are reached (ca. 10–11 m), a period of more rapid sedimentation is implied, though the statistical over-

Table 1 New ¹⁴C ages, prepared using the ABA-SC and ABOX-SC techniques[a]

Depth, m	Lab code (ANUA-)	Uncorrected %M (±1σ)	BP (±1σ)
ABA-SC			
1.55	15508	30.47 ± 0.43	9,600 ± 115
2.05	11524	28.22 ± 0.69	10,200 ± 200
4.60	11523	6.56 ± 0.38	22,130 + 500 −470
6.75	11522	2.83 ± 0.22	29,230 + 720 −660
7.55	11509	3.30 ± 0.10	27,900 + 290 −280
8.95	11525	1.40 ± 0.14	35,550 + 1060 −940
10.85	14120	0.56 ± 0.05	45,270 + 1780 −1450
12.50	11520	0.57 ± 0.07	44,980 + 2300 −1790
14.45	15506	0.54 ± 0.04	45,640 + 1740 −1430
15.90	11519	0.46 ± 0.07	47,860 + 3530 −2440
20.00	**12306**	**0.20 ± 0.06**	**'Background'**
ABOX-SC			
1.55	11518	30.32 ± 1.28	9,640 ± 340
2.05	11517	30.64 ± 1.42	9,560 ± 370
6.75	11516	2.54 ± 0.18	30,170 + 670 −620
7.55	11515	3.20 ± 0.23	28,180 + 660 −610
8.95	11514	1.71 ± 0.15	33,680 + 880 −800
10.85	11513	0.56 ± 0.10	45,130 + 3030 −2200
12.50	15507	0.71 ± 0.04	42,430 + 1200 −1040
14.45	13406	0.23 ± 0.07	>48,700
15.90	(13402	3.69 ± 0.70)	
	13403	0.64 ± 0.10	43,620 + 2410 −1850
20.00	**12305**	**0.67 ± 0.11**	**'Background'?**

[a]In calculating the ¹⁴C ages, a background of 0.20 ± 0.07 %M has been subtracted from the uncorrected values in column 3. A $\delta^{13}C$ value of −25‰ was assumed. All measurements were carried out on the 850 °C fraction from the stepped combustion procedure with the exception of the value in parentheses for the 15.90 m ABOX-pretreated sample which is the 630 °C fraction, and the 20 m ABOX-pretreated sample for which the 630 and 850 °C fractions were combined.

lap of the ages precludes developing a robust age-depth relationship for the lower part of the sequence. This period corresponds with a major transition from lake to swamp sediments, when sedimentation rates may have been particularly high, a proposal supported by very low pollen concentrations within the sediment matrix (P Moss, unpublished data).

Intriguingly, the ABOX-SC ages are considerably more variable below 10–11 m than the ABA-SC method, though above this depth, the different pretreatment methods provide virtually indistinguishable ages, indicating any pervasive contamination is relatively small compared to the quantity of contemporaneous "charcoal" and bulk sediment present in the sample. It has been demonstrated that the ABOX-SC technique more effectively decontaminates charcoal samples than conventional treatments within paleosol and cave contexts (Bird et al. 1999; Turney et al. 2001). Within the sediments of Lynch's Crater, considerably lower ¹⁴C activity can be obtained from ABOX-SC treated samples stratigraphically higher in the sequence (as low as 0.23 pMC at 14.45 m, c.f. 0.67 pMC at 20.0 m,
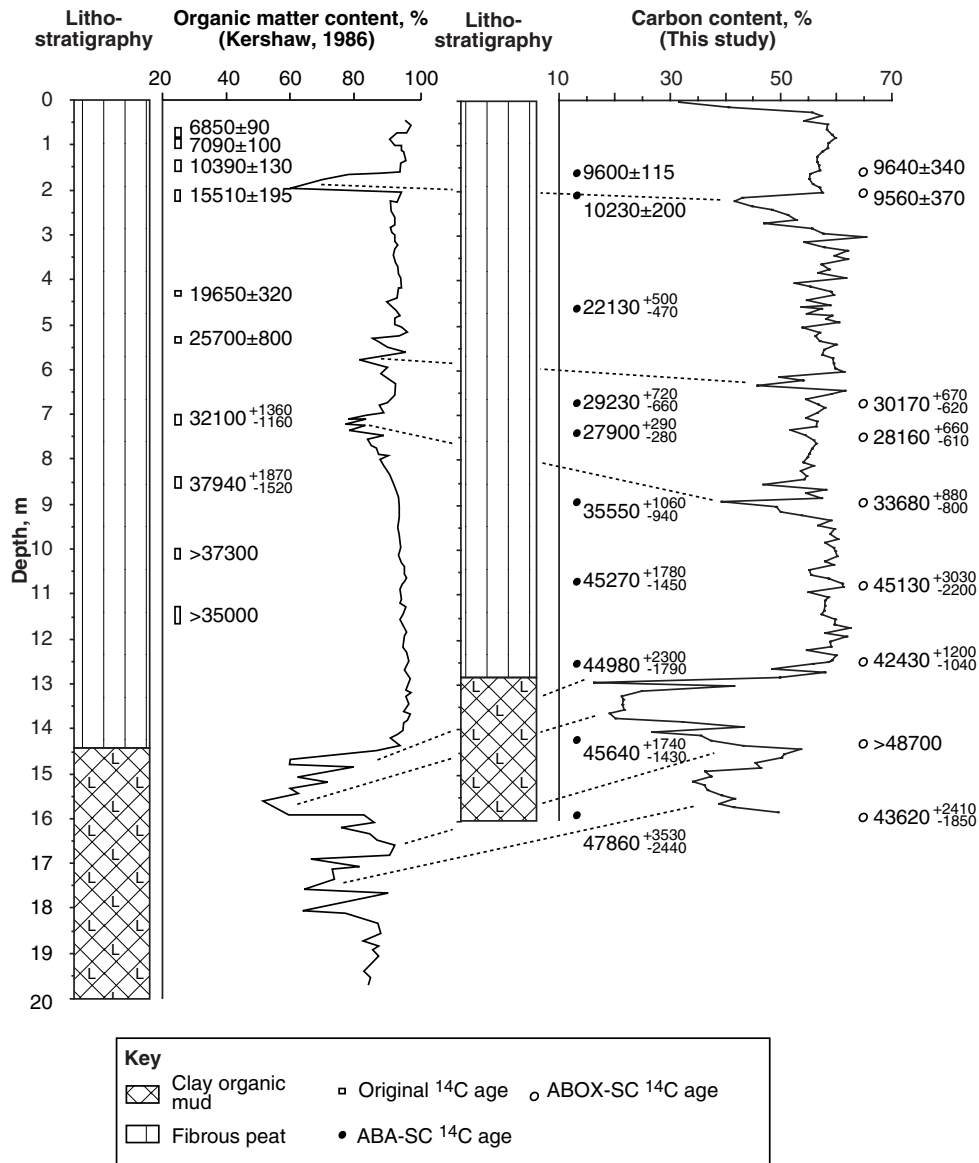
Figure 3 Organic carbon content (determined using an elemental analyzer) and organic matter content of the original core reported by Kershaw (1986). Dashed lines indicate points of correlation between cores. Open boxes, untreated ^{14}C ages (Kershaw 1986); open circles, ABOX-SC ^{14}C ages (this study); closed circles, ABA-SC ^{14}C ages (this study).

Table 1) and suggests that the ABOX-SC technique may not be the best method to employ for fine-grained, "charcoal-poor" sediments, and may in fact concentrate small quantities of younger contaminants along with fine grained "charcoal" in the sediments. Bird and Gröcke (1997) found that dichromate oxidation alone could not completely oxidize some non-charcoal carbon from marine sediments, and used an additional base oxidation step to fully remove this contamination. They postulated that the carbon might be derived from bacterial material, which is highly resistant to oxidative degradation in acid solutions.
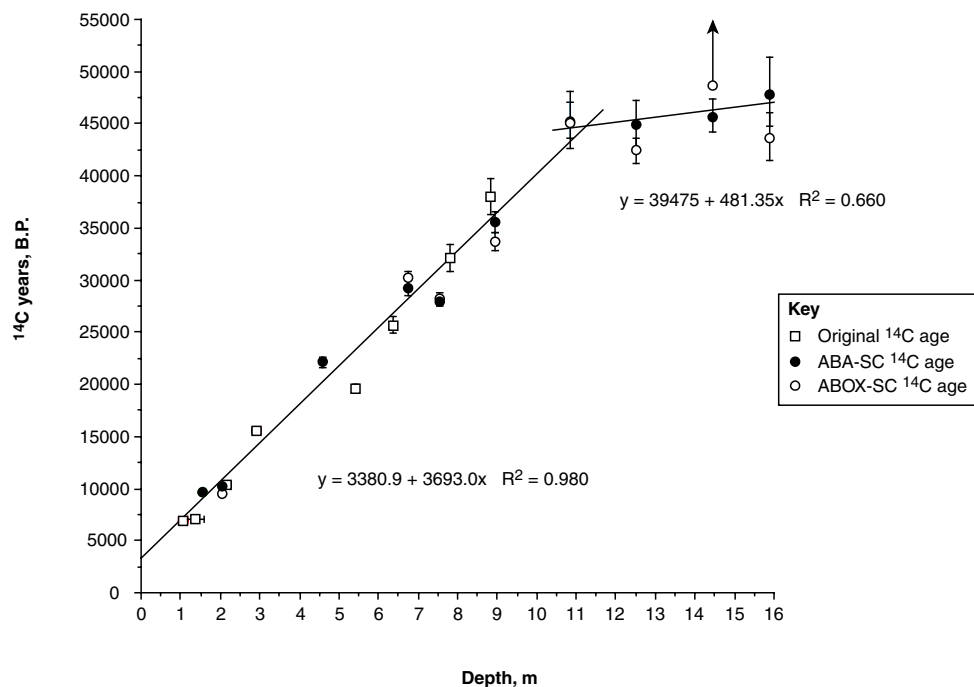
Figure 4 Comparison between the ^{14}C ages reported from Lynch's Crater. Best-fit lines were developed using the ABA-SC ^{14}C ages.

The persistence of younger bacterial carbon (from bacteria which colonized the sediments subsequent to their deposition) through the ABOX pretreatment might explain the variable, ^{14}C activities recorded in samples towards the base of the sequence. This younger carbon may be concentrated during the pretreatment along with the small amount of fine "charcoal" in the sediments and would contribute to the observed background. Alternatively, "charcoal" of relatively younger age may be vertically displaced within the sedimentary profile but this is considered unlikely here as little evidence of such a mechanism is apparent in the ABA-SC ages. Variations in the magnitude of contamination may explain the larger degree of scatter in the ABOX-SC ages towards the base of the core (reflecting the variable length of time in dichromate and the differing proportions of younger carbon in the sediments) than is apparent in the ABA-SC ages.

The results indicate therefore that the ABOX-SC pretreatment may not be the most reliable technique for removing contaminants from lake and peat sediments, unless "charcoal" is present in sufficiently large enough quantities for complete pretreatment. As a result of the problematic nature of confidently assigning a background to the individual ABOX-SC age measurements, we have derived a new chronology for Lynch's Crater based on the ABA-SC ages that appear to be more robust (Figure 4). The uppermost 11 m of peat sediments record a linear, relatively slow sedimentation rate (~0.3 m ka^{-1}) back to ~45,000 BP. Below this depth to 16 m (~48,000 BP), the sedimentation rate appears to be significantly more rapid (2.1 m ka^{-1}), though the ages derived using ABA-SC are statistically indistinguishable, precluding a precise age-depth relationship.

CONCLUSION

This study has demonstrated that the original untreated ^{14}C ages reported for Lynch's Crater are reliable to the depth at which they reached background for that system, suggesting an almost linear sedimentation rate over this interval. However, the newly determined ^{14}C ages, using the ABA-SC and ABOX-SC pretreatments, indicate a significant increase in sedimentation rate below this depth. In addition, the background for the ABOX-SC technique does appear to be more variable and higher than the more conventional ABA-SC technique. The results therefore suggest that the ABOX-SC pretreatment may not be the most reliable technique for removing contaminants from lake and peat sediments, unless "charcoal" is present in large enough quantities to allow the sample to be subjected to the full period in the oxidizing solution and still provide enough material for target preparation. For bulk sediment samples, the ABA-SC pretreatment appears to be the more reliable methodology for samples in the >40 ka BP time range. The implications of these results for interpreting the vegetation records and the timing of human activity in the local area will be discussed elsewhere (Turney et al., in preparation).

ACKNOWLEDGMENTS

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