TOWARDS A RADIOCARBON CHRONOLOGY OF THE LATE-GLACIAL: SAMPLE SELECTION STRATEGIES

M J C Walker[1] • C Bryant[2] • G R Coope[3] • D D Harkness[4] • J J Lowe[3] • E M Scott[5]

ABSTRACT. This paper outlines a dating program designed to test the reproducibility of radiocarbon dates on different materials of Late-Glacial age (plant macrofossils, fossil beetle remains, and the "humic" and "humin" chemical fractions of limnic sediments) using a combination of radiometric (beta counting) and accelerator mass spectrometry (AMS) techniques. The results have implications for the design of sampling strategies and for the development of improved dating protocols, both of which are important if a high-precision ^{14}C chronology for the Late-Glacial is to be achieved.

INTRODUCTION

The transition from the last glacial to the present interglacial (the "Last Termination" or "Late-Glacial") is one of the most intensively studied episodes in the entire Quaternary. The stratigraphic record of this period is of particular interest to Quaternary science for it constitutes the best archive of the way in which earth and atmospheric processes interact during the transition from a cold ("glacial") to a warm ("interglacial") stage (Lowe and Walker 1997). A range of dating methods has been applied to this period, but by far the most widely used has been radiocarbon, and in Europe and North America, and indeed in other areas of the world also, the time-scale for environmental change during the Late-Glacial and early Holocene rests very largely on ^{14}C dating (see e.g. Lowe 1994; Walker 1995). Until the late 1980s, the majority of Late-Glacial dates were obtained by beta counting of samples of organic lake muds, but the preferred strategy now is to date plant macrofossil material by accelerator mass spectrometry (AMS). This is partly because AMS offers the prospect of dating at a much higher level of stratigraphic resolution (since it is possible to obtain dates on very small samples of material), and partly because of the widely held view that AMS dates on plant macrofossils are inherently more reliable than those obtained from the sediment matrix, as the carbon sources of the former are known and they are not composed of heterogeneous material that could be of different ages (see Lowe and Walker 2000).

Recent work in the British Isles, however, has revealed a number of problems with ^{14}C dating the Late-Glacial, for while coherent chronologies have been obtained from some sites using either AMS (e.g. Preece 1994, Lowe et al. 1995) or a combination of radiometric and AMS ^{14}C dating (e.g. Switsur and Housley 1998), inconsistencies are evident in other dating series (e.g. Lowe et al. 1988; Walker et al. in preparation). AMS ^{14}C dates on macrofossils have frequently proved to be younger than radiometric ages from the corresponding sediment matrix, a discrepancy that has usually been attributed to the influence of older carbon residues in limnic deposits (Lowe 1991). Yet there are sequences where a coherent time-scale for the Late-Glacial has been obtained from radiometric dates on bulk sediment samples, but where AMS ^{14}C dates on plant macrofossils appear to be aberrant (e.g. Walker et al, in preparation). Equally, there are other dating series where there are variations in age not only between the AMS and radiometric dates, but also between AMS ^{14}C dates on different plant macrofossils from the same stratigraphic horizons (Turney et al. 2000). These results

[1]Department of Archaeology, University of Wales, Lampeter, Wales SA48 7ED, United Kingdom.
Email: walker@lamp.ac.uk.
[2]NERC Radiocarbon Laboratory, East Kilbride, Glasgow G75 OQF, United Kingdom
[3]Department of Geography, Royal Holloway, University of London, Egham, Surrey TW20 0EX, United Kingdom
[4]Scottish Universities Environmental Research Centre, East Kilbride, Glasgow G75 0QF, United Kingdom
[5]Department of Statistics, University of Glasgow, Glasgow G12 8QW, United Kingdom

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suggest, therefore, that while AMS ^{14}C dating of macrofossil materials *may* offer the potential for providing a more securely-based time-scale than the radiometric dating of lake sediments, a critical re-appraisal of both approaches may now be required if a reliable ^{14}C chronology for the Late-Glacial is to be developed.

AIMS AND HYPOTHESES

One way in which an evaluation of the two techniques can be carried out is to compare radiometric and AMS ^{14}C dates from the same stratigraphic horizons within a single Late-Glacial profile. Comparative ^{14}C dating of bulk sediment samples and plant macrofossils has previously been undertaken, for example at sites in The Netherlands (Törnqvist et al. 1992) and in Norway (Birks et al. 1996; Gulliksen et al. 1998), although these have been on samples of Holocene age. For the Late-Glacial, there are sites where different materials (sediments, plant macrofossils, etc.) have been dated (e.g. Böttger et al. 1998; Hoek et al. 1999) but, as far as can be established, no *systematic* comparative ^{14}C dating programme has yet been undertaken on materials of Late-Glacial age. The aim of the present project is therefore to compare radiometric and AMS ^{14}C dates on samples taken from two Late-Glacial profiles in northern Britain; St Bees in Cumbria, and Sluggan Bog in Northern Ireland. The specific hypotheses to be tested are:

1. Statistically similar ^{14}C ages can be obtained on organic sediments using radiometric (beta counting) and AMS methods,
2. Plant macrofossils from the same stratigraphic horizon dated by AMS produce ^{14}C ages that are statistically indistinguishable from those obtained from the associated sediment matrix,
3. AMS ^{14}C dates obtained on other organic media (e.g. Coleoptera) are statistically indistinguishable from AMS dates on plant macrofossils recovered from the same stratigraphic horizons,
4. Coleoptera from the same stratigraphic horizons, but from different ecological niches, have comparable ^{14}C ages.

In this paper we present the results from the St. Bees site only. The data from Sluggan will be discussed elsewhere.

THE SITE

The site of St. Bees is located on the Cumbrian coast of northwest England (Figure 1) where the infilling of a kettle hole formed in Late Devensian till has been exposed in section by cliff erosion. The underlying bedrock is Triassic sandstone. The sedimentary sequence at the sampling point comprises, from the base, a lower sand unit, 50 cm of organic limnic sediment and over 2 m of cryoturbated minerogenic sediments. This succession is capped by a thin Holocene peat and blown sand. Previous work at the site, involving both pollen and coleopteran analysis (Walker 1956; Pearson 1962; Coope and Joachim 1980; Coope 1994), showed the sequence to be of Late-Glacial age, with the organic limnic sediments having accumulated during the Late-Glacial Interstadial (Greenland Interstadial 1/GI-1 of Björck et al. 1998 and Walker et al. 1999), while the overlying cryoturbated sediments are attributable to the Loch Lomond/Younger Dryas Stadial (Greenland Stadial 1/GS-1).

FIELD AND LABORATORY METHODS

The field program was driven by two overriding imperatives: first, high-resolution sampling of closely constrained horizons was essential, and second, in order that ^{14}C dates could be obtained from a range of materials, large quantities of sediment were required from each sampling horizon. Accordingly, a field strategy was devised whereby the sediments overlying the Late-Glacial Intersta-

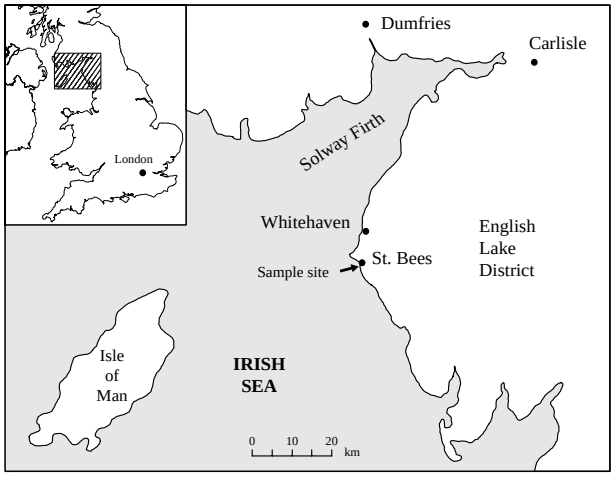

Figure 1 Location of the Late-Glacial site at St. Bees

dial organic sediments were cut back by a least 50 cm to expose the top of the sequence. Successive sediment increments, each measuring 2 cm in thickness, were then extracted sequentially down through the profile. A minimum of 1 kg of material was obtained from each sampling horizon. Vertical monoliths (10 ×10 × 50 cm) were also taken for pollen and LOI (loss-on-ignition) analysis.

In the laboratory, samples for LOI and for pollen analysis were removed from the monoliths at 1 cm intervals, and prepared using standard techniques (Bengtsson and Enell 1986; Moore et al. 1991). These data provide a litho- and biostratigraphic context for the ^{14}C dated-horizons. Samples for ^{14}C dating were taken from the 2 cm thick bulk sediment samples. Further sub-samples were then sieved and plant macrofossils remains, principally seeds of Cyperaceae (*Carex*, *Eleocharis*, and *Scirpus*) and lignified plant remains, were recovered.

Previous studies had shown that the Late-Glacial Interstadial sediments at St. Bees contained a diverse fossil coleopteran fauna (Pearson 1962; Coope and Joachim 1980). There are relatively few published reports of ^{14}C dating of fossil insect remains (e.g. Elias and Toolin 1990; Elias et al. 1991, Törnqvist et al. 1992, Cong et al. 1996), and there are none from British contexts. Fossil Coleoptera have proved to be extremely valuable proxy indicators of Late-Glacial climate (e.g. Atkinson et al. 1987; Coope et al. 1998), and hence the possibility of obtaining AMS ^{14}C ages on fossil Coleoptera constituted a potentially valuable new avenue of enquiry. Careful extraction and identification of the coleopteran remains from selected 2 cm samples provided species-specific samples of insect remains for dating. Although this approach inevitably produced very small samples of material and, in some instances, either a carbon yield too low for dating purposes or resultant ages with relatively large quoted errors (see below), it was felt to be worth pursuing, because of the possibility of obtaining ^{14}C dates on insects of known trophic position in the environment.

Samples for radiometric dating were prepared in the NERC Radiocarbon Laboratory at East Kilbride, under the laboratory's routine quality control procedures. The total organic content in each of the bulk sediment samples for radiometric dating was separated quantitatively into alkali soluble (humic) and alkali insoluble (humin) fractions. This enabled an assessment of the amount of any mineral (essentially ^{14}C free) carbon contained within the sediment matrix. Each sample was subjected to two digestions in 2M KOH (80 °C for 24 hr). The alkali-soluble fraction recovered was fil-

tered, centrifuged to remove particulates, and acidified to precipitate the "humic" fraction. This was recovered by centrifugation, washed to neutral pH and dried to constant weight in a drying oven. The "humin" fraction was acidified with 2M HCL (80° C for 24 hr), washed to neutral pH, and filtered and dried to constant weight in a drying oven. The radiometric dating programme followed routine procedures to prepare benzene for beta counting (Harkness and Wilson 1972) and employed ultra-low level scintillation spectrometry. The quantitative recovery of "humic" carbon ranged between 3 and 20% by weight of the dried raw sediment. Yields of "humin" carbon were lower, in the range 2 to 11%. Nevertheless, these components were recovered in sufficient quantity to allow the preparation of between 0.7 and 4.0 mL of benzene for radiomeric counting. In selected instances, a mg-scaled separation was undertaken to allow direct, but totally independent, age comparison via ^{14}C AMS analysis.

Other sediment components for AMS dating (mainly plant macrofossils and Coleoptera) were digested in mineral acid (2M HCL) and then washed to neutral pH. Targets for AMS measurement were prepared in East Kilbride, with quantitative recovery of the component fraction carbon by combustion in a sealed quartz tube, followed by cryogenic separation of the product CO_2 (Boutton et al. 1983). Aliquots of the CO_2 were converted to an iron/graphite mix (Fe:C<3:1 by weight) using a Fe/Zn reduction procedure (Slota et al. 1987). Where available sample sizes were <0.5 mg C, additional background and known-age reference standards were prepared in the same sizes as the constrained samples, so that appropriate background corrections could be applied and tested. Batches of prepared targets (comprising samples plus their counterpart quality assurance and reference standards) were passed either to the NSF Accelerator Facility at the University of Arizona (Donahue 1990), or to the Lawrence Livermore Laboratory, California (Southon et al. 1990), for isotope mass analysis. The plant macrofossils and Coleoptera fragments yielded relatively high carbon contents, typically in the range 40 to 54% by weight. However, only the former were available in sufficient quantity to enable the preparation of optimally sized graphite targets, i.e. containing about 1.3 mg C, and with sufficient excess CO_2 for independent measurement of the ^{13}C enrichment. Beetle fragments were much less plentiful and the carbon recovered for graphite production was restricted to somewhere between 0.15 and 0.5 mg per sample target. This analytical constraint is reflected in the relative magnitudes of the 1σ confidence intervals calculated for individual age measurements.

RESULTS

Pollen and LOI Data

The principal features of the new St. Bees pollen diagram (Figure 2) are 1) the predominance of herbaceous taxa and the limited representation of woody tax below 25 cm, 2) the expansion of tree birch from 25 cm upwards, and 3) the expansion of aquatic flora (principally *Myriophyllum*) in the upper part of the diagram. Comparisons with other sites in north-west Britain (e.g. Walker 1966, Pennington 1970, 1977; Johnson et al. 1972) suggest that the middle and later part of the Late-Glacial Interstadial are recorded in the sequence. The LOI record (Figure 2) is notable for two episodes of reduced organic content. The first at around 14.5 cm finds no clear parallels in the pollen record, whereas the second at about 28.5 cm is accompanied by a slight and short-lived decline in both *Betula* and *Juniperus* values. The dates from both the "humic" and plant macrofossil series (Table 1) place the latter in the time interval 11,900–12,100 ^{14}C BP, broadly equivalent to GI-1d (Older Dryas) of Björck et al. (1998).

Depth (cm)	"Humic" age		"Humin" age		Weighted mean age	Plant macrofossils		Coleoptera	
48	SRR-6310 CAMS-57200	10,790 ± 50 10,710 ± 40	SRR-6311	11,265 ± 50	11,305 ± 50	CAMS-43634	10,850 ± 60[a]		
44	SRR-6308	10,865 ± 45	SRR-6309	11,430 ± 65	10,970 ± 50	CAMS-43633	11,020 ± 60[a]	AA-32320	10,195 ± 80[7]
38	SRR-6306 CAMS-57199	11,285 ± 45 11,210 ± 45	SRR-6307	11,515 ± 60	11,330 ± 50	CAMS-43632	11,180 ± 60[a]		
32	SRR-6304	11,860 ± 45	SRR-6305	12,670 ± 95	12,005 ± 55	CAMS-43631	11,700 ± 60[a]		
31						CAMS-45850	12,140 ± 70[e]		
28	SRR-6302	12,155 ± 45	SRR-6303	12,320 ± 80	12,185 ± 55	CAMS-43630	11,940 ± 60[b]		
22	SRR-6300	12,375 ± 55	SRR-6301	12,625 ± 45	12,535 ± 50	CAMS-43629	12,180 ± 60[b]	CAMS-52330 AA-32318 AA-32319	10,640 ± 120[1] 11,190 ± 85[2] 11,535 ± 95[3]
18	SRR-6298 CAMS-57198	12,530 ± 45 12,400 ± 50	SRR-6299	12,945 ± 115	12,610 ± 60	CAMS-43628 CAMS-59480	12,230 ± 60[b] 12,240 ± 40[d]	CAMS-50389 CAMS-50388 CAMS-50387	11,850 ± 80[1] 12,160 ± 80[2] 12,160 ± 80[3]
12	SRR-6296	12,400 ± 45	SRR-6297	13,110 ± 70	12,585 ± 55	CAMS-43627	11,590 ± 60[c]	CAMS-52329 CAMS-52328 AA-32316 AA-32317	10,940 ± 180[4] 11,370 ± 180[1] 11,780 ± 85[2] 11,860 ± 110[3]
8	SRR-6294 CAMS-57197	12,375 ± 45 12,290 ± 50	SRR-6295	12,645 ± 65	12,440 ± 50	CAMS-43626	12,230 ± 60[c]	CAMS-52323 CAMS-52324 CAMS-52325 CAMS-52326 CAMS-52327	10,270 ± 210[3] 11,000 ± 170[1] 11,340 ± 140[6] 11,600 ± 140[5] 11,750 ± 120[8]
4	SRR-6292	12,435 ± 45	SRR-6293	12,765 ± 75	12,505 ± 55	CAMS-43625	12,240 ± 60[c]	CAMS-52331 CAMS-52332	9390 ± 220[6] 11,410 ± 110[2]
1	SRR-6290	12,305 ± 45	SRR-6291	12,935 ± 70	12,460 ± 55	CAMS-43624 SRR-6322 SRR-6323	12,020 ± 60[c] 11,820 ± 60[f] 12,420 ± 105[g]		
–0.50	SRR-6289 CAMS-57196	11,870 ± 120 12,270 ± 50	AA-30939	16,150 ± 160	13,060 ± 135	CAMS-43623	12,030 ± 60[c]		
–7						CAMS-45848	12,230 ± 60[e]		

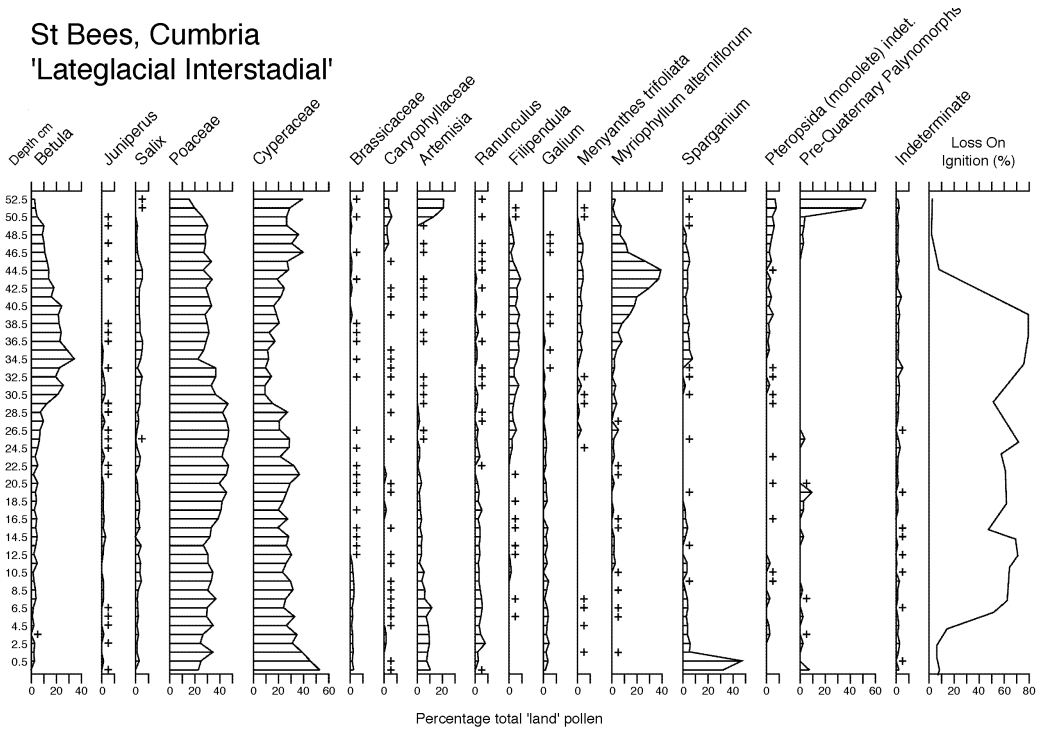

Figure 2 Late-Glacial Interstadial percentage pollen diagram from St. Bees (principal taxa only), and loss-on-ignition (LOI) values

Radiocarbon Dates

The ^{14}C data-set from St. Bees (Table 1) is the most comprehensive to be obtained from any Late-glacial sequence in Britain. It comprises 12 "humic" and 12 "humin" ages on bulk sediment samples, plus the associated weighted means; 18 AMS dates on different terrestrial plant macrofossils; and 18 AMS dates on fossil coleopteran fragments. In addition, "humic" fractions from the material of 5 samples prepared for radiometric dating have been dated by AMS.

Within most levels of the St. Bees profile, there is a significant scatter of ^{14}C age values that often exceeds the quantifiable limits of analytical confidence (quoted here at the 1σ level). However, there does appear to be an underlying age/depth pattern (Figure 3) that is indicative of either an initial period of relatively rapid sedimentation, or a progressive temporal decline in atmospheric ^{14}C concentration (a ^{14}C plateau) that coincides with changes in carbon isotope geochemistry during the middle and later part of the Late-Glacial Interstadial. Intercomparisons between the St. Bees record and that from Sluggan (unpublished) may eventually shed further light on this matter.

In all levels within the profile, the "humin" carbon yielded ages that are older than the stratigraphically contemporaneous "humic" fraction (Figures 3a and 3b). Although the local bedrock probably contains little, if any, older carbonaceous material, Carboniferous strata outcrop to the north and northwest of St. Bees. Hence, fragments of coal may well have been carried south-eastwards by Irish Sea ice and subsequently incorporated into the limnic deposits of the kettle hole. The influence of reworked mineral carbon in these particular Late-Glacial sediments is reflected in the older "humin" age values. Clearly, therefore, the "weighted mean" age profile (Figure 3c), consisting of ^{14}C ages

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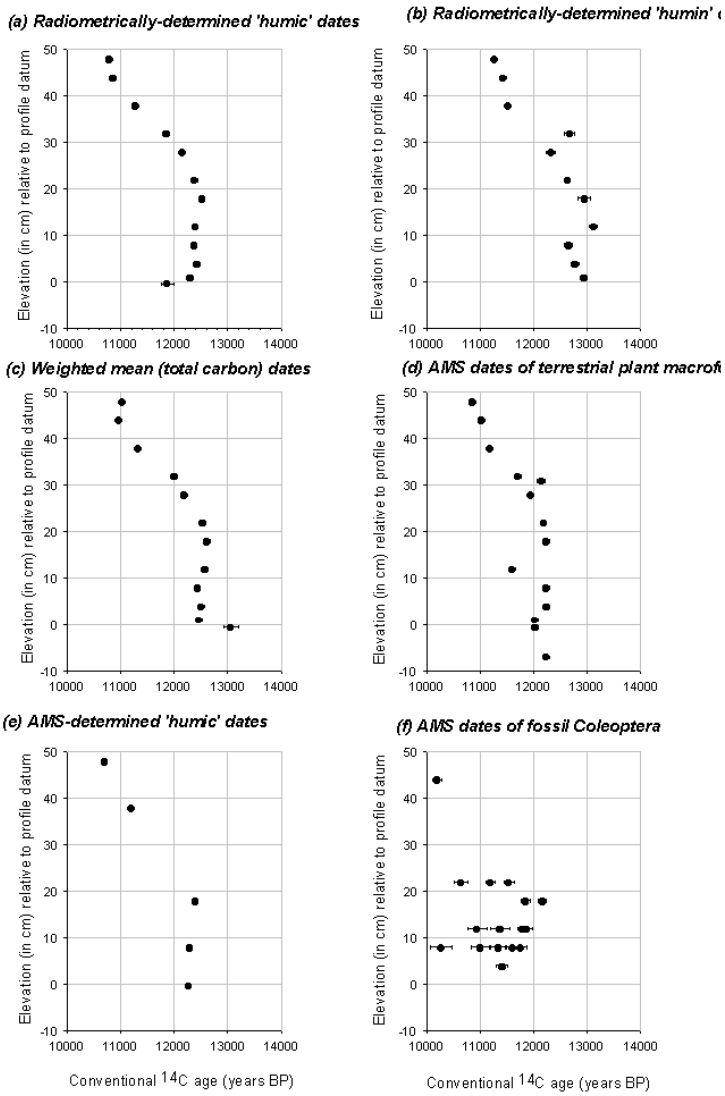

Figure 3 Age depth profile for different materials from St. Bees: (a) radiometrically-determined "humic" dates; (b) radiometrically-determined "humin" dates; (c) weighted mean (total carbon) dates; (d) AMS dates of terrestrial plant macrofossils; (e) AMS-determined "humic" dates; (f) AMS dates of fossil Coleoptera

derived from total and/or acid washed carbon from the bulk sediment samples, does not provide a satisfactory basis for a Late-Glacial chronology for this site.

The terrestrial plant macrofossil AMS ages (Figure 3d) follow closely the radiometrically determined ages for the "humic" sediment fraction, with nine of the twelve horizons showing no statistically significant difference between "humic" and plant macrofossil age. This confirms the findings of Gullikesen et al. (1998) from the Kråkenes site in western Norway, where NaOH extracts from early Holocene algal gyttjas yielded ages that were consistent with those derived from terrestrial plant mac-

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rofossils. At St. Bees, a quadratic curve can be fitted to the two dating series with R^2 values in excess of 90%, demonstrating a consistency in pattern between the "humic" and plant macrofossil results. However, even where the two analytical strategies produced statistically concordant values, i.e. overlapping within the 95% (2σ) confidence envelopes, the macrofossil ages are invariably younger by about 75 ^{14}C yr. Over all the horizons, the average younging effect in the plant macrofossils is in the order of about 160 ^{14}C yr. Working on the premise that differences associated with the isotope measurement procedures can be discounted, there are two possible explanations for this discrepancy: 1) that the "humic" ages may reflect a small, but significant, component from the older mineral carbon in these sediments, or 2) plant macrofossils can incorporate trace amounts of modern carbon, probably during the initial extraction and/or pretreatment stages of their analysis. In an attempt to resolve this problem, five sub-samples of bulk sediment were taken from those levels recording the greatest convergence and also maximum divergence in ages between the "humic" and plant macrofossil age profiles. These were pretreated on a size scale comparable with that used for the macrofossil fragments, and the recovered "humic" carbon was dated by AMS. The results (Figure 3e; Table 1, SRR/CAMS values, column 1) show no statistically significant difference although, with the exception of the sample from –0.5 cm, the AMS ages display a tendency to slightly younger median values.

In the context of working hypothesis 2 above, four points emerge from these results. First, it would seem reasonable to infer that the existing "humic" and terrestrial plant macrofossil curves from St. Bees are likely to represent the respective maximum and minimum limits of the true ^{14}C chronological record; second, the close similarity between the radiometrically determined "humic" ages and the majority of the AMS plant macrofossil dates suggests that terrestrially derived macrofossils *can* produce an internally consistent chronology for the Late-Glacial; third, a coherent chronology *can* be obtained from the "humic" fraction of Late-Glacial limnic sediments, the component that, particularly in the dating of peats, has tended to be discarded in preference to the "humin" fraction; fourth, the broad measure of agreement between the radiometric and AMS dates on the "humic" sediment fractions demonstrates that closely comparable dates can be obtained on lake sediments (albeit, on the "humic" fraction only) using both radiometric and AMS methods (cf. Birks et al. 1996; Gulliksen et al. 1998).

One feature of the plant macrofossil data that perhaps merits further comment is the dating of seeds of *Potamogeton* from 18 cm in the profile. These were chosen for dating principally because an age determination was also being obtained from this horizon on a species of beetle that feeds exclusively on *Potamogeton natans* (see below). Previous workers have tended to avoid *Potamogeton* seeds as a medium for ^{14}C dating, as some species of this aquatic plant have submerged leaves, and hence subaquatic photosynthesis might introduce a hard-water error into subsequent ^{14}C dates (see e.g. Törnqvist et al. 1992). In this case, however, the date on the *Potamogeton* seeds (12,240 ± 40 BP) is virtually identical to that obtained from the terrestrial seeds of *Scirpus* and *Carex* (12,230 ± 60 BP) but, perhaps more significantly, is almost 300 yr *younger* than the "humic" age determination from the same horizon. Clearly, therefore, there can be no hard-water error in this particular case. While this might have been anticipated given the nature of the bedrock geology of the site (see above), it has been suggested that glacial till may also contain older inert carbon, and that this becomes available for synthesis in recently deglaciated aquatic environments, even where there is no obvious source of older carbon in the local bedrock (Sutherland 1980). The Potamogetonaceae are a large family, and it is not certain which species was dated here, although in view of its widespread occurrence, there must be a strong possibility that the seeds are from *P. natans*. *Potamogeton* seeds are common macrofossils in many Late-Glacial sediment sequences, and while only one age determination was made on *Potamogeton* from the St. Bees profile, this result does suggest that seeds of *Potamogeton* may

be unaffected by a hard water factor in areas not only where limestone or ancient carbonate carbon is absent from the catchment, but also where lakes developed on a substrate of glacial till.

Eight species of Coleoptera, each with distinctive ecological affinities, were selected for ^{14}C dating (Table 2). However, the results of this part of the experimental dating programme have been variable (Figure 3f). In level 18 cm, for example, dates have been obtained on three different fossil beetle species which are closely comparable with plant macrofossil age determinations. Indeed two of the three beetle dates are statistically indistinguishable at 1σ from the dates on the terrestrial plant macrofossils (Table 1). Curiously, the coleopteran species that feeds exclusively on *P. natans*, *Donacia versicolorea*, produced a ^{14}C age that was younger (by almost 400 years) than the age on the seeds of *Potamogeton*. The date on the aquatic beetle was, in turn, almost 300 years younger than the dates on the two terrestrial taxa (*Adoxus obscurus* and *Barynotus squamosus*) although their ages do just overlap at the 2σ level of confidence. Like the *Potamogeton* seeds, therefore, the beetle chitin shows no evidence of a hard-water factor.

Table 2 ^{14}C dated Coleoptera from St. Bees and their ecological affinities

Donacia versicolorea	An aquatic species living exclusively on *Potamogeton natans*
Adoxus obscurus	A terrestrial species feeding exclusively on *Epilobium*
Barynotus squamosus	A terrestrial species: larvae eat roots of herbaceous vegetation; adults climb trees to eat leaves
Byrrhus sp.	A terrestraial feeders on moss (not *Sphagnum*)
Carabus problematicus	A terrestrial carnivore: feeds on worms and small insect larvae
Plagiodora versicolorea	A species feeding exclusively on *Salix* (also *Populus*)
Otiorhynchus nodosus	similar in appearance to *Barynotus*; a leaf feeder-larvae feed underground on roots
Agabus bipustulatus	An aquatic carnivore: feeds exclusively on range of aquatic animals

Elsewhere, however, the dating results are more problematical, partly because of the very large errors on some of the dates as a consequence of small sample size and commensurately low carbon yield, partly because of significant differences in age between beetle dates from the same sample horizon, and partly because of marked differences in ages between the insect dates and those obtained from other media. In the sample from 12 cm, three of the four insect dates are statistically indistinguishable (at 2σ) from the date on plant macrofossils, although it should be noted that this is one of the horizons where there is a clear discrepancy between the plant macrofossil and "humic" age determination. Indeed, in spite of the relatively large confidence ranges, all four insect dates are significantly younger (at 2σ) than the "'humic" age measurement. In the other four horizons from which coleopteran dates have been obtained, the insect dates (despite large errors on some) are statistically significantly younger than both the plant macrofossil and "humic" age determinations from those horizons. Interestingly, a similar age discrepancy between plant macrofossils and coleopteran remains was noted by Elias et al. (1991).

Why this should be so is not at all clear. Dating was carried out on very small samples of material and hence there are the inevitable problems of high background ^{14}C and the difficulties of quantifying this background, although targets of background material were prepared in sizes comparable with those of the samples. Nevertheless, this cannot account for the apparently consistent pattern in relative order of age of the respective insect species (Table 1). In levels 12, 18, and 22 cm, for example, *Donacia versicolorea* is younger in each case than *Adoxus obscurus* which, in turn, in two of the levels is younger than *Barynotus squamosus* and of an identical age in the third. Although this pat-

tern does not appear in a fourth sample (8 cm), where *Barynotus* is younger than *Donacia*, these dates were on such small samples of material (<200 µg) that they may be of lesser significance. It seems equally unlikely that there is a taphonomic problem involving, for example, translocation of younger material down through the profile, for while beetle chitin is relatively durable, the fossil coleopteran remains are small, and would be unlikely to survive reworking. Moreover, such a process again cannot offer a reasonable explanation for the observed pattern of ^{14}C ages of the coleopteran fossils in each particular horizon. An alternative hypothesis, therefore, is that the age variation is in some way related to the biochemistry of the fossil chitin, possibly involving the post-mortem incorporation of younger organic residues into the polysaccharide lattice. Independently derived results (Hodgins (2001) highlight the fact that a significant age difference can exist between the carbon recovered from the amino acid and polysaccharide components in a specific sample of fossil exoskeleton. The partial replacement of structural amino acids by counterpart biochemical groups derived from the surrounding sediment would seem to be a possible mechanism here. Although speculative, this proposed biochemical exchange could go some way towards explaining the apparent species-related pattern of the younging effect described above. The clear physical different in exoskeleton structure between particular insect species and/or fragments, for example surface area to weight ratios, could be a significant factor in determining their susceptibility to post-mortem diagenesis. Clearly, further work is now needed on the nature of beetle chitin in order to explore further the ramifications of this hypothesis (see Hodgins 2001).

Two significant points emerge from this aspect of the dating program. First, it is evident that, in certain circumstances and providing that sufficient material can be obtained, meaningful ^{14}C dates *can* be obtained on species-specific samples of fossil insects, Second, the age discrepancies between Coleoptera and other materials, notably plant macrofossils and "humic" sediment fractions, suggests that a diagenetic factor (resulting in younger ages) might affect insect chitin, and that this may be more pronounced in some species than in others. The implication is that the dating of aggregate samples of insect remains (e.g. Cong et al. 1996) would almost certainly produce erroneous ^{14}C ages. Furthermore, if post-depositional diagenetic changes are registered in the the insect chitin residues, the possibility cannot be excluded that similar processes might also affect plant macrofossil remains, particularly the macromolecular outer surface of seeds. This could be one explanation for the small offset in age between the plant macrofossil and "humic" age determinations referred to above.

CONCLUSIONS

The following conclusions all have implications for the design of ^{14}C dating strategies for the Late-Glacial:

1. The evidence from this tightly constrained sampling programme on Late-Glacial limnic sediments shows that AMS ^{14}C dates from the same stratigraphic horizon are comparable to the radiometric results, but the data emphasise the critical importance of careful sampling in the selection of material for both AMS and radiometric dating.
2. The data not only confirm the view that the "weighted mean" ages of bulk sediment samples from Late-Glacial limnic contexts are likely to be aberrant, but also raise serious doubts about the value of the "humin" sediment fraction (which, hitherto, has been the most widely used component) in the dating of Late-Glacial events (e.g. Walker and Harkness 1990).
3. By contrast, the evidence from St. Bees suggests that, as was shown to be the case with early Holocene gyttjas (Gulliksen et al. 1998), ^{14}C dates on the "humic" sediment fraction *can* pro-

vide a coherent time-scale for Late-Glacial limnic sequences. This is important because, if replicated in other profiles, it means that a viable ^{14}C chronology can still be obtained from Late-Glacial sediments, even when (as is often the case) plant macrofossils are absent.

4. There is a broad measure of agreement in the *trend* between radiometric dates on the "humic" fraction of Late-Glacial sediments and the AMS ^{14}C age determinations on terrestrial plant macrofossils from the same stratigraphic horizon. However, there is a small, but significant (and consistent) difference in age between the plant macrofossils (younger) and the "humic" values (older). This tendency is also evident in direct intercomparisons between paired AMS and radiometric age determinations from the "humic" carbon.
5. While some of the coleopteran dates from the St. Bees sequence are comparable with independent age measurements from the same stratigraphic horizon (on terrestrial macrofossils and on the "humic" fraction of the sediment matrix), other dates are clearly aberrant. It seems unlikely that this is a product of taphonomic processes, but post-depositional diagenetic influences on the insect chitin could be a significant factor. Further work is now required on the biochemistry of insect chitin in order to explore this hypothesis. The results of such work could have important implications for the ^{14}C dating not only of fossil insect remains, but possibly also for the dating of plant macrofossils.

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